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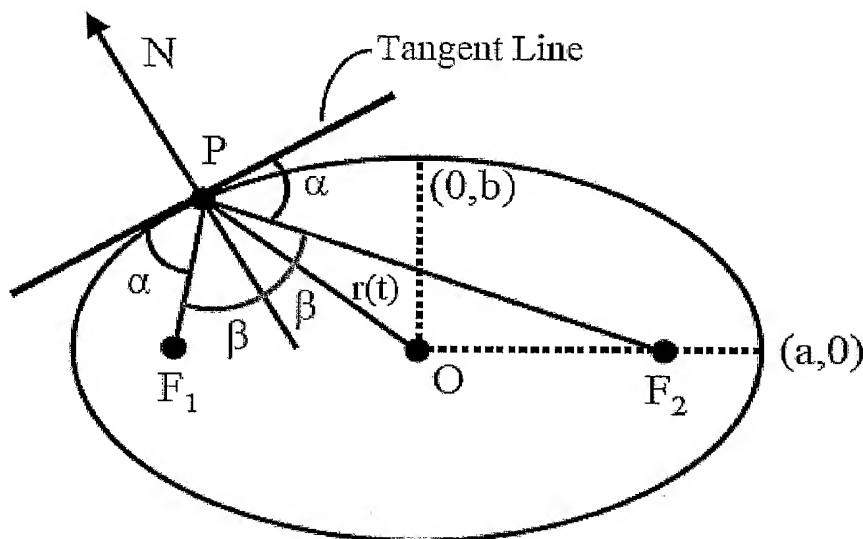
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(54) Title: SYSTEM AND METHOD OF COMPUTING AND RENDERING THE NATURE OF POLYATOMIC MOLECULES AND POLYATOMIC MOLECULAR IONS



(57) Abstract: A method and system of physically solving the charge, mass, and current density functions of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species using Maxwell's equations and computing and rendering the physical nature of the chemical bond using the solutions. The results can be displayed on visual or graphical media. The display can be static or dynamic such that electron motion and specie's vibrational, rotational, and translational motion can be displayed in an embodiment. The displayed information is useful to anticipate reactivity and physical properties. The insight into the nature of the chemical bond of at least one specie can permit the solution and display of those of other species to provide utility to anticipate their reactivity and physical properties.

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# SYSTEM AND METHOD OF COMPUTING AND RENDERING THE NATURE OF POLYATOMIC MOLECULES AND POLYATOMIC MOLECULAR IONS

This application claims priority to U.S. Application Nos.: 60/730,882, filed October 28,  
5 2005; 60/732,154, filed November 2, 2005; 60/737,744, filed November 18, 2005;  
60/758,528, filed January 13, 2006; 60/780,518, filed March 9, 2006; 60/788,694, filed April  
4, 2006; 60/812,590, filed June 12, 2006; and 60/815,253, June 21, 2006, the complete  
disclosures of which are incorporated herein by reference.

## 10 Field of the Invention:

This invention relates to a system and method of physically solving the charge, mass,  
and current density functions of polyatomic molecules, polyatomic molecular ions, diatomic  
molecules, molecular radicals, molecular ions, or any portion of these species, and computing  
and rendering the nature of these species using the solutions. The results can be displayed on  
15 visual or graphical media. The displayed information provides insight into the nature of these  
species and is useful to anticipate their reactivity, physical properties, and spectral absorption  
and emission, and permits the solution and display of other species.

Rather than using postulated unverifiable theories that treat atomic particles as if they  
were not real, physical laws are now applied to atoms and ions. In an attempt to provide  
20 some physical insight into atomic problems and starting with the same essential physics as  
Bohr of the  $e^-$  moving in the Coulombic field of the proton with a true wave equation, as  
opposed to the diffusion equation of Schrödinger, a classical approach is explored which  
yields a model that is remarkably accurate and provides insight into physics on the atomic  
level. The proverbial view deeply seated in the wave-particle duality notion that there is no  
25 large-scale physical counterpart to the nature of the electron is shown not to be correct.  
Physical laws and intuition may be restored when dealing with the wave equation and  
quantum atomic problems.

Specifically, a theory of classical quantum mechanics (CQM) was derived from first  
principles as reported previously [reference Nos. 1-8] that successfully applies physical laws  
30 to the solution of atomic problems that has its basis in a breakthrough in the understanding of  
the stability of the bound electron to radiation. Rather than using the postulated Schrödinger  
boundary condition: " $\Psi \rightarrow 0$  as  $r \rightarrow \infty$ ", which leads to a purely mathematical model of the  
electron, the constraint is based on experimental observation. Using Maxwell's equations, *the*

*classical wave equation is solved with the constraint that the bound  $n = 1$ -state electron cannot radiate energy.* Although it is well known that an accelerated *point* particle radiates, an *extended distribution* modeled as a superposition of accelerating charges does not have to radiate. A simple invariant physical model arises naturally wherein the predicted results are  
5 extremely straightforward and internally consistent requiring minimal math, as in the case of the most famous equations of Newton, Maxwell, Einstein, de Broglie, and Planck on which the model is based. No new physics is needed; only the known physical laws based on direct observation are used.

Applicant's previously filed WO2005/067678 discloses a method and system of  
10 physically solving the charge, mass, and current density functions of atoms and atomic ions and computing and rendering the nature of these species using the solutions. The complete disclosure of this published PCT application is incorporated herein by reference.

Applicant's previously filed WO2005/116630 discloses a method and system of  
physically solving the charge, mass, and current density functions of excited states of atoms  
15 and atomic ions and computing and rendering the nature of these species using the solutions. The complete disclosure of this published PCT application is incorporated herein by reference.

Applicant's previously filed U.S. Published Patent Application No. 20050209788A1,  
relates to a method and system of physically solving the charge, mass, and current density  
20 functions of hydrogen-type molecules and molecular ions and computing and rendering the nature of the chemical bond using the solutions. The complete disclosure of this published application is incorporated herein by reference.

### Background of the Invention

25 The old view that the electron is a zero or one-dimensional point in an all-space probability wave function  $\Psi(x)$  is not taken for granted. The theory of classical quantum mechanics (CQM), derived from first principles, must successfully and consistently apply physical laws on all scales [1-8]. Stability to radiation was ignored by all past atomic models. Historically, the point at which QM broke with classical laws can be traced to the issue of  
30 nonradiation of the one electron atom. Bohr just postulated orbits stable to radiation with the further postulate that the bound electron of the hydrogen atom does not obey Maxwell's equations—rather it obeys different physics [1-12]. Later physics was replaced by "pure mathematics" based on the notion of the inexplicable wave-particle duality nature of electrons

which lead to the Schrödinger equation wherein the consequences of radiation predicted by Maxwell's equations were ignored. Ironically, Bohr, Schrödinger, and Dirac used the Coulomb potential, and Dirac used the vector potential of Maxwell's equations. But, all ignored electrodynamics and the corresponding radiative consequences. Dirac originally attempted to solve the bound electron physically with stability with respect to radiation according to Maxwell's equations with the further constraints that it was relativistically invariant and gave rise to electron spin [13]. He and many founders of QM such as Sommerfeld, Bohm, and Weinstein wrongly pursued a planetary model, were unsuccessful, and resorted to the current mathematical-probability-wave model that has many problems [9-16]. Consequently, Feynman for example, attempted to use first principles including Maxwell's equations to discover new physics to replace quantum mechanics [17].

Physical laws may indeed be the root of the observations thought to be "purely quantum mechanical", and it was a mistake to make the assumption that Maxwell's electrodynamic equations must be rejected at the atomic level. Thus, in the present approach, the classical wave equation is solved with the constraint that a bound  $n = 1$ -state electron cannot radiate energy.

Herein, derivations consider the electrodynamic effects of moving charges as well as the Coulomb potential, and the search is for a solution representative of the electron wherein there is acceleration of charge motion without radiation. The mathematical formulation for zero radiation based on Maxwell's equations follows from a derivation by Haus [18]. The function that describes the motion of the electron must not possess spacetime Fourier components that are synchronous with waves traveling at the speed of light. Similarly, nonradiation is demonstrated based on the electron's electromagnetic fields and the Poynting power vector.

It was shown previously [1-8] that CQM gives closed form solutions for the atom including the stability of the  $n = 1$  state and the instability of the excited states, the equation of the photon and electron in excited states, and the equation of the free electron and photon, which predict the wave particle duality behavior of particles and light. The current and charge density functions of the electron may be directly physically interpreted. For example, spin angular momentum results from the motion of negatively charged mass moving systematically, and the equation for angular momentum,  $\mathbf{r} \times \mathbf{p}$ , can be applied directly to the wave function (a current density function) that describes the electron. The magnetic moment of a Bohr magneton, Stern Gerlach experiment, g factor, Lamb shift, resonant line width and

shape, selection rules, correspondence principle, wave particle duality, excited states, reduced mass, rotational energies, and momenta, orbital and spin splitting, spin-orbital coupling, Knight shift, and spin-nuclear coupling, and elastic electron scattering from helium atoms, are derived in closed-form equations based on Maxwell's equations. The calculations agree with experimental observations.

The Schrödinger equation gives a vague and fluid model of the electron. Schrödinger interpreted  $e\Psi^*(x)\Psi(x)$  as the charge-density or the amount of charge between  $x$  and  $x + dx$  ( $\Psi^*$  is the complex conjugate of  $\Psi$ ). Presumably, then, he pictured the electron to be spread over large regions of space. After Schrödinger's interpretation, Max Born, who was working with scattering theory, found that this interpretation led to inconsistencies, and he replaced the Schrödinger interpretation with the probability of finding the electron between  $x$  and  $x + dx$  as

$$\int \Psi(x)\Psi^*(x) dx \quad (1)$$

Born's interpretation is generally accepted. Nonetheless, interpretation of the wave function is a never-ending source of confusion and conflict. Many scientists have solved this problem by conveniently adopting the Schrödinger interpretation for some problems and the Born interpretation for others. This duality allows the electron to be everywhere at one time—yet have no volume. Alternatively, the electron can be viewed as a discrete particle that moves here and there (from  $r = 0$  to  $r = \infty$ ), and  $\Psi\Psi^*$  gives the time average of this motion.

In contrast to the failure of the Bohr theory and the nonphysical, adjustable-parameter approach of quantum mechanics, multielectron atoms [1, 4] and the nature of the chemical bond [1, 5] are given by exact closed-form solutions containing fundamental constants only. Using the nonradiative wave equation solutions that describe the bound electron having conserved momentum and energy, the radii are determined from the force balance of the electric, magnetic, and centrifugal forces that corresponds to the minimum of energy of the system. The ionization energies are then given by the electric and magnetic energies at these radii. The spreadsheets to calculate the energies from exact solutions of one through twenty-electron atoms are given in '06 Mills GUT [1] and are available from the internet [19]. For 400 atoms and ions, as well as hundreds of molecules, the agreement between the predicted and experimental results is remarkable.

The background theory of classical quantum mechanics (CQM) for the physical solutions of atoms and atomic ions is disclosed in R. Mills, *The Grand Unified Theory of*

*Classical Quantum Mechanics*, January 2000 Edition, BlackLight Power, Inc., Cranbury, New Jersey, (" '00 Mills GUT"), provided by BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ, 08512; R. Mills, *The Grand Unified Theory of Classical Quantum Mechanics*, September 2001 Edition, BlackLight Power, Inc., Cranbury, New Jersey, Distributed by Amazon.com (" '01 Mills GUT"), provided by BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ, 08512; R. Mills, *The Grand Unified Theory of Classical Quantum Mechanics*, July 2004 Edition, BlackLight Power, Inc., Cranbury, New Jersey, (" '04 Mills GUT"), provided by BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ, 08512; R. Mills, *The Grand Unified Theory of Classical Quantum Mechanics*, January 2005 Edition, BlackLight Power, Inc., Cranbury, New Jersey, (" '05 Mills GUT"), provided by BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ, 08512 (posted at [www.blacklightpower.com](http://www.blacklightpower.com)); R. L. Mills, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834, (" '06 Mills GUT"), provided by BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ, 08512 (posted at <http://www.blacklightpower.com/bookdownload.shtml>); in prior PCT applications PCT/US02/35872; PCT/US02/06945; PCT/US02/06955; PCT/US01/09055; PCT/US01/25954; PCT/US00/20820; PCT/US00/20819; PCT/US00/09055; PCT/US99/17171; PCT/US99/17129; PCT/US 98/22822; PCT/US98/14029; PCT/US96/07949; PCT/US94/02219; PCT/US91/08496; PCT/US90/01998; and PCT/US89/05037 and U.S. Patent No. 6,024,935; the entire disclosures of which are all incorporated herein by reference (hereinafter "Mills Prior Publications").

The following list of references, which are also incorporated herein by reference in their entirety, are referred to in the above sections using [brackets]:

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#### SUMMARY OF THE INVENTION

The present invention, an exemplary embodiment of which is also referred to as Millsian software, stems from a new fundamental insight into the nature of the atom. Applicant's new theory of Classical Quantum Mechanics (CQM) reveals the nature of atoms and molecules using classical physical laws for the first time. As discussed above, traditional quantum mechanics can solve neither multi-electron atoms nor molecules exactly. By contrast, CQM produces exact, closed-form solutions containing physical constants only for even the most complex atoms and molecules.

10 The present invention is the first and only molecular modeling program ever built on the CQM framework. All the major functional groups that make up most organic molecules have been solved exactly in closed-form solutions with CQM. By using these functional groups as building blocks, or independent units, a potentially infinite number of organic molecules can be solved. As a result, the present invention can be used to visualize the exact 3D structure and calculate the heat of formation of almost any organic molecule.

20 For the first time, the significant building-block molecules of chemistry have been successfully solved using classical physical laws in exact closed-form equations having fundamental constants only. The major functional groups have been solved from which molecules of infinite length can be solved almost instantly with a computer program. The predictions are accurate within experimental error for over 375 exemplary molecules.

25 Applicant's CQM is the theory that physical laws (Maxwell's Equations, Newton's Laws, Special and General Relativity) must hold on all scales. The theory is based on an often overlooked result of Maxwell's Equations, that an extended distribution of charge may, under certain conditions, accelerate without radiating. This "condition of no radiation" is invoked to solve the physical structure of subatomic particles, atoms, and molecules.

30 In exact closed-form equations with physical constants only, solutions to thousands of known experimental values arise that were beyond the reach of previous outdated theories. These include the electron spin, g-factor, multi-electron atoms, excited states, polyatomic molecules, wave-particle duality and the nature of the photon, the masses and families of

fundamental particles, and the relationships between fundamental laws of the universe that reveal why the universe is accelerating as it expands. CQM is successful to over 85 orders of magnitude, from the level of quarks to the cosmos. Applicant now has over 65 peer-reviewed journal articles and also books discussing the CQM and supporting experimental evidence.

5       The molecular modeling market was estimated to be a two-billion-dollar per year industry in 2002, with hundreds of millions of government and industry dollars invested in computer algorithms and supercomputer centers. This makes it the largest effort of computational chemistry and physics.

10       The present invention's advantages over other models includes: Rendering true molecular structures; Providing precisely all characteristics, spatial and temporal charge distributions and energies of every electron in every bond, and of every bonding atom; Facilitating the identification of biologically active sites in drugs; and Facilitating drug design.

15       An objective of the present invention is to solve the charge (mass) and current-density functions of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species from first principles. In an embodiment, the solution for the polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species is derived from Maxwell's equations invoking the constraint that the bound electron before excitation does  
20       not radiate even though it undergoes acceleration.

25       Another objective of the present invention is to generate a readout, display, or image of the solutions so that the nature of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species be better understood and potentially applied to predict reactivity and physical and optical properties.

30       Another objective of the present invention is to apply the methods and systems of solving the nature of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species and their rendering to numerical or graphical form to all atoms and atomic ions.

      These objectives and other objectives are obtained by a system of computing and rendering the nature of at least one specie selected from a group of diatomic molecules having at least one atom is other than hydrogen, polyatomic molecules, molecular ions, polyatomic molecular ions, or molecular radicals, or any functional group therein, comprising



physical, Maxwellian solutions of charge, mass, and current density functions of said specie, said system comprising processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie; and an output device in communication with the processing means for displaying said physical, Maxwellian  
5 solutions of charge, mass, and current density functions of said specie.

Also provided is a composition of matter comprising a plurality of atoms, the improvement comprising a novel property or use discovered by calculation of at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density  
10 functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.

The presented exact physical solutions for known species of the group of polyatomic  
15 molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any functional group therein, can be applied to other species. These solutions can be used to predict the properties of other species and engineer compositions of matter in a manner which is not possible using past quantum mechanical techniques. The molecular solutions can be used to design synthetic pathways and predict product yields based on  
20 equilibrium constants calculated from the heats of formation. Not only can new stable compositions of matter be predicted, but now the structures of combinatorial chemistry reactions can be predicted.

Pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of  
25 the specie to be identified from the common spatial charge-density functions of a series of active species. Novel drugs can now be designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the drug.

The system can be used to calculate conformations, folding, and physical properties, and the exact solutions of the charge distributions in any given specie are used to calculate the  
30 fields. From the fields, the interactions between groups of the same specie or between groups on different species are calculated wherein the interactions are distance and relative orientation dependent. The fields and interactions can be determined using a finite-element-analysis approach of Maxwell's equations.

Embodiments of the system for performing computing and rendering of the nature of the polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species using the physical solutions may comprise a general purpose computer. Such a general purpose computer may have any  
 5 number of basic configurations. For example, such a general purpose computer may comprise a central processing unit (CPU), one or more specialized processors, system memory, a mass storage device such as a magnetic disk, an optical disk, or other storage device, an input means, such as a keyboard or mouse, a display device, and a printer or other output device. A system implementing the present invention can also comprise a special  
 10 purpose computer or other hardware system and all should be included within its scope.

Although not preferred, any of the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm 10\%$ , if desired.

#### BRIEF DESCRIPTION OF THE DRAWINGS

15

Fig. 1 illustrates an elliptical current element of the prolate spheroidal MO;

Fig. 2 illustrates the ellipsoidal current-density surface obtained by stretching  $Y_0^0(\theta, \phi)$  along the semimajor axis;

Fig. 3 illustrates the angular momentum components of the MO and S;

20

Fig. 4 illustrates cross section of an atomic orbital;

Fig. 5 illustrates A. Prolate spheroid MO;

Fig. 6 illustrates the equilateral triangular  $H_3^+(1/p)$ ;

Fig. 7 illustrates the cross section of the OH MO;

Fig. 8 illustrates OH MO comprising the superposition of the  $H_2$ -type ellipsoidal MO and  
 25 the  $O2p_y$  AO with a relative charge-density of 0.75 to 1.25;

Fig. 9 illustrates  $H_2O$  MO comprising the linear combination of two O-H-bond MOs;

Fig. 10 illustrates the cross section of the NH MO showing the axes, angles, and point of intersection of the  $H_2$ -type ellipsoidal MO with the  $N2p_x$  AO;

Fig. 11 illustrates NH MO comprising the superposition of the  $H_2$ -type ellipsoidal MO and  
 30 the  $N2p_x$  AO with a relative charge-density of 0.75 to 1.25;

Fig. 12 illustrates  $NH_2$  MO comprising the linear combination of two N-H-bond MOs;

- Fig. 13 illustrates  $NH_3$  MO comprising the linear combination of three  $N-H$  -bonds;
- Fig. 14 illustrates the cross section of the  $CH$  MO showing the axes, angles, and point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  HO;
- Fig. 15 illustrates  $CH$  MO comprising the superposition of the  $H_2$ -type ellipsoidal MO and  
5 the  $C2sp^3$  HO with a relative charge-density of 0.75 to 1.25;
- Fig. 16 illustrates  $CH_2$  MO comprising the linear combination of two  $C-H$  -bond MOs;
- Fig. 17 illustrates  $CH_3$  MO comprising the linear combination of three  $C-H$  -bond MOs;
- Fig. 18 illustrates  $CH_4$  MO comprising the linear combination of four  $C-H$  -bond MOs  
formed by the superposition of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO;
- 10 Fig. 19 illustrates the cross section of the  $N_2$  MO;
- Fig. 20 illustrates  $N_2$  MO comprising the  $\sigma$  MO ( $H_2$ -type MO) with  $N$  atoms at the foci;
- Fig. 21 illustrates the cross section of the  $O_2$  MO;
- Fig. 22 illustrates  $O_2$  MO comprising the  $\sigma$  MO ( $H_2$ -type MO);
- Fig. 23 illustrates the cross section of the  $F_2$  MO;
- 15 Fig. 24 illustrates  $F_2$  MO comprising the  $\sigma$  MO ( $H_2$ -type MO) with  $F$  atoms at the foci;
- Fig. 25 illustrates the cross section of the  $Cl_2$  MO;
- Fig. 26 illustrates  $Cl_2$  MO comprising the superposition of the  $H_2$ -type ellipsoidal MO and  
the two  $Cl3sp^3$  HOs;
- Fig. 27 illustrates the cross section of the  $CN$  MO;
- 20 Fig. 28 illustrates  $CN$  MO;
- Fig. 29 illustrates the cross section of the  $CO$  MO;
- Fig. 30 illustrates  $CO$  MO;
- Fig. 31 illustrates the cross section of the  $NO$  MO;
- Fig. 32 illustrates  $NO$  MO;
- 25 Fig. 33 illustrates the cross section of the  $CO_2$  MO;
- Fig. 34 illustrates  $CO_2$  MO;
- Fig. 35 illustrates the cross section of the  $NO_2$  MO;
- Fig. 36 illustrates  $NO_2$  MO;
- Fig. 37 illustrates the cross section of the  $C-C$  -bond MO ( $\sigma$  MO) and one  $C-H$  -bond

MO of ethane;

Fig. 38 illustrates the cross section of one  $C-H$ -bond MO of ethane showing the axes,

angles, and point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{ethane} 2sp^3$

HO;

5 Fig. 39 illustrates  $CH_3CH_3$  MO comprising the linear combination of two sets of three

$C-H$ -bond MOs and a  $C-C$ -bond MO;

Fig. 40 illustrates the cross section of the  $C=C$ -bond MO ( $\sigma$  MO) and one  $C-H$ -bond

MO of ethylene showing the axes, angles, and point of intersection of each  $H_2$ -type

ellipsoidal MO with the corresponding  $C_{ethylene} 2sp^3$  HO;

10 Fig. 41 illustrates the cross section of one  $C-H$ -bond MO of ethylene showing the axes,

angles, and point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{ethylene} 2sp^3$

HO;

Fig. 42 illustrates  $CH_2CH_2$  MO comprising the linear combination of two sets of two

$C-H$ -bond MOs and a  $C=C$ -bond MO;

15 Fig. 43 illustrates the cross section of the  $C\equiv C$ -bond MO ( $\sigma$  MO) and one  $C-H$ -bond

MO of acetylene showing the axes, angles, and point of intersection of each  $H_2$ -type

ellipsoidal MO with the corresponding  $C_{acetylene} 2sp^3$  HO;

Fig. 44 illustrates  $CHCH$  MO comprising the linear combination of two  $C-H$ -bond MOs

and a  $C\equiv C$ -bond MO;

20 Fig. 45 illustrates the cross section of one  $C=C$ -bond MO ( $\sigma$  MO) and one  $C-H$ -bond

MO of benzene showing the axes, angles, and point of intersection of each  $H_2$ -type

ellipsoidal MO with the corresponding  $C_{benzene} 2sp^3$  HO;

Fig. 46 illustrates the cross section of one  $C-H$ -bond MO of benzene showing the axes,

angles, and point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{benzene} 2sp^3$

HO;

25

Fig. 47 illustrates  $C_6H_6$  MO comprising the linear combination of six sets of  $C-H$ -bond

MOs bridged by  $C=C$ -bond MOs;

Fig. 48 illustrates the cross section of one  $C-C$ -bond MO ( $\sigma$  MO) and one  $C-H$ -bond

MO of  $C_nH_{2n+2}$  showing the axes, angles, and point of intersection of each  $H_2$ -type

ellipsoidal MO with the corresponding  $C_{alkane} 2sp^3$  HO;

30

Fig. 49 illustrates the cross section of one  $C-H$ -bond MO of  $C_nH_{2n+2}$  showing the axes, angles, and point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{alkane} 2sp^3$  HO;

Fig. 50 illustrates  $C_3H_8$  MO comprising a linear combination of  $C-H$ -bond MOs and  
5  $C-C$ -bond MOs of the two methyl groups and one methylene group;

Fig. 51 illustrates  $C_4H_{10}$  MO comprising a linear combination of  $C-H$ -bond MOs and  
 $C-C$ -bond MOs of the two methyl and two methylene groups;

Fig. 52 illustrates  $C_5H_{12}$  MO comprising a linear combination of  $C-H$ -bond MOs and  
 $C-C$ -bond MOs of the two methyl and three methylene groups;

10 Fig. 53 illustrates  $C_6H_{14}$  MO comprising a linear combination of  $C-H$ -bond MOs and  
 $C-C$ -bond MOs of the two methyl and four methylene groups;

Fig. 54 illustrates  $C_7H_{16}$  MO comprising a linear combination of  $C-H$ -bond MOs and  
 $C-C$ -bond MOs of the two methyl and five methylene groups;

Fig. 55 illustrates  $C_8H_{18}$  MO comprising a linear combination of  $C-H$ -bond MOs and  
15  $C-C$ -bond MOs of the two methyl and six methylene groups;

Fig. 56 illustrates  $C_9H_{20}$  MO comprising a linear combination of  $C-H$ -bond MOs and  
 $C-C$ -bond MOs of the two methyl and seven methylene groups. (A) Opaque view  
of the charge-density of the  $C-C$ -bond and  $C-H$ -bond MOs;

Fig. 57 illustrates  $C_{10}H_{22}$  MO comprising a linear combination of  $C-H$ -bond MOs and  
20  $C-C$ -bond MOs of the two methyl and eight methylene groups;

Fig. 58 illustrates  $C_{11}H_{24}$  MO comprising a linear combination of  $C-H$ -bond MOs and  
 $C-C$ -bond MOs of the two methyl and nine methylene groups;

Fig. 59 illustrates  $C_{12}H_{26}$  MO comprising a linear combination of  $C-H$ -bond MOs and  
 $C-C$ -bond MOs of the two methyl and ten methylene groups;

25 Fig. 60 illustrates  $C_{18}H_{38}$  MO comprising a linear combination of  $C-H$ -bond MOs and  
 $C-C$ -bond MOs of the two methyl and sixteen methylene groups;

Fig. 61.A illustrates 1,3 Butadiene;

Fig. 61.B illustrates 1,3 Pentadiene;

Fig. 61.C illustrates 1,4 Pentadiene;

30 Fig. 61.D illustrates 1,3 Cyclopentadiene;

Fig. 61E illustrates Cyclopentene;

Fig. 62 illustrates Naphthalene;

Fig. 63 illustrates Toluene;

Fig. 64 illustrates Benzoic acid;

5 Fig. 65 illustrates Pyrrole;

Fig. 66 illustrates Furan;

Fig. 67 illustrates Thiophene;

Fig. 68 illustrates Imidazole;

Fig. 69 illustrates Pyridine;

10 Fig. 70 illustrates Pyrimidine;

Fig. 71 illustrates Pyrazine;

Fig. 72 illustrates Quinoline;

Fig. 73 illustrates Isoquinoline;

Fig. 74 illustrates Indole;

15 Fig. 75 illustrates Adenine;

Fig. 76 illustrates a block diagram of an exemplary software program; and

Figs. 77 and 78 illustrate pictures of an exemplary software program.

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# Section I

## THE NATURE OF THE CHEMICAL BOND OF HYDROGEN-TYPE MOLECULES AND MOLECULAR IONS

5

With regard to the Hydrino Theory—BlackLight Process section, the possibility of states with  $n = 1/p$  is also predicted in the case of hydrogen molecular species wherein  $H(1/p)$  reacts a proton or two  $H(1/p)$  atoms react to form  $H_2^+(1/p)$  and  $H_2(1/p)$ , respectively. The natural molecular-hydrogen coordinate system based on symmetry is ellipsoidal coordinates.

10 The magnitude of the central field in the derivations of molecular hydrogen species is taken as the general parameter  $p$  wherein  $p$  may be an integer which may be predictive of new possibilities. Thus,  $p$  replaces the effective nuclear charge of quantum mechanics and corresponds to the physical field of a resonant photon superimposed with the field of the proton. The case with  $p = 1$  is evaluated and compared with the experimental results for  
15 hydrogen species in Table 11.1, and the consequences that  $p = \text{integer}$  are considered in the Nuclear Magnetic Resonance Shift section.

Two hydrogen atoms react to form a diatomic molecule, the hydrogen molecule.

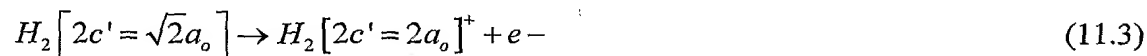


where  $2c'$  is the internuclear distance. Also, two hydrino atoms react to form a diatomic  
20 molecule, a dihydrino molecule.

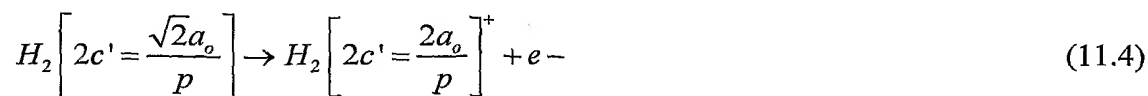


where  $p$  is an integer.

Hydrogen molecules form hydrogen molecular ions when they are singly ionized.



25 Also, dihydrino molecules form dihydrino molecular ions when they are singly ionized.



## HYDROGEN-TYPE MOLECULAR IONS

Each hydrogen-type molecular ion comprises two protons and an electron where the equation of motion of the electron is determined by the central field which is  $p$  times that of a proton at each focus ( $p$  is one for the hydrogen molecular ion, and  $p$  is an integer greater than one for each  $H_2^+(1/p)$ , called dihydrino molecular ion). The differential equations of motion in the case of a central field are [1]

$$m(\ddot{r} - r\dot{\theta}^2) = f(r) \quad (11.5)$$

$$m(2\dot{r}\dot{\theta} + r\ddot{\theta}) = 0 \quad (11.6)$$

The second or transverse equation, Eq. (11.6), gives the result that the angular momentum is constant.

$$r^2\dot{\theta} = \text{constant} = L/m \quad (11.7)$$

where  $L$  is the angular momentum ( $\hbar$  in the case of the electron). The central force equations can be transformed into an orbital equation by the substitution,  $u = \frac{1}{r}$ . The differential equation of the orbit of a particle moving under a central force is

$$\frac{\partial^2 u}{\partial \theta^2} + u = -\frac{1}{mL^2 u^2} f(u^{-1}) \quad (11.8)$$

Because the angular momentum is constant, motion in only one plane need be considered; thus, the orbital equation is given in polar coordinates. The solution of Eq. (11.8) for an inverse-squared force

$$f(r) = -\frac{k}{r^2} \quad (11.9)$$

is

$$r = r_0 \frac{1+e}{1+e \cos \theta} \quad (11.10)$$

$$e = A \frac{m \frac{L^2}{m^2}}{k} \quad (11.11)$$

$$r_0 = \frac{m \frac{L^2}{m^2}}{k(1+e)} \quad (11.12)$$



where  $e$  is the eccentricity of the ellipse and  $A$  is a constant. The equation of motion due to a central force can also be expressed in terms of the energies of the orbit. The square of the speed in polar coordinates is

$$v^2 = (\dot{r}^2 + r^2 \dot{\theta}^2) \quad (11.13)$$

- 5 Since a central force is conservative, the total energy,  $E$ , is equal to the sum of the kinetic,  $T$ , and the potential,  $V$ , and is constant. The total energy is

$$\frac{1}{2} m (\dot{r}^2 + r^2 \dot{\theta}^2) + V(r) = E = \text{constant} \quad (11.14)$$

Substitution of the variable  $u = \frac{1}{r}$  and Eq. (11.7) into Eq. (11.14) gives the orbital energy equation.

$$10 \quad \frac{1}{2} m \frac{L^2}{m^2} \left( \frac{\partial^2 u}{\partial \theta^2} + u^2 \right) + V(u^{-1}) = E \quad (11.15)$$

Because the potential energy function  $V(r)$  for an inverse-squared force field is

$$V(r) = -\frac{k}{r} = -ku \quad (11.16)$$

the energy equation of the orbit, Eq. (11.15),

$$\frac{1}{2} m \frac{L^2}{m^2} \left( \frac{\partial^2 u}{\partial \theta^2} + u^2 \right) - ku = E \quad (11.17)$$

- 15 which has the solution

$$r = \frac{m \frac{L^2}{m^2} k^{-1}}{1 + \left( 1 + 2Em \frac{L^2}{m^2} k^{-2} \right)^{1/2} \cos \theta} \quad (11.18)$$

where the eccentricity,  $e$ , is

$$e = \left( 1 + 2Em \frac{L^2}{m^2} k^{-2} \right)^{1/2} \quad (11.19)$$

- Eq. (11.19) permits the classification of the orbits according to the total energy,  $E$ , as  
20 follows:

$E < 0,$	$e < 1$	closed orbits (ellipse or circle)
$E = 0,$	$e = 1$	parabolic orbit
$E > 0,$	$e > 1$	hyperbolic orbit

Since  $E = T + V$  and is constant, the closed orbits are those for which  $T < |V|$ , and the open orbits are those for which  $T \geq |V|$ . It can be shown that the time average of the kinetic energy,  $\langle T \rangle$ , for elliptical motion in an inverse-squared field is  $1/2$  that of the time average of the magnitude of the potential energy,  $\langle |V| \rangle$ .  $\langle T \rangle = 1/2 \langle |V| \rangle$  [1].

5 As demonstrated in the One-Electron Atom section, the electric inverse-squared force is conservative; thus, the angular momentum of the electron,  $\hbar$ , and the energy of atomic orbitspheres are constant. In addition, the orbitspheres are nonradiative when the boundary condition is met.

The central force equation, Eq. (11.14), has orbital solutions, which are circular,  
10 elliptical, parabolic, or hyperbolic. The former two types of solutions are associated with atomic and molecular orbitals. These solutions are nonradiative. The boundary condition for nonradiation given in the One-Electron Atom section, is the absence of components of the spacetime Fourier transform of the current-density function synchronous with waves traveling at the speed of light. The boundary condition is met when the velocity for the charge density  
15 at every coordinate position on the orbitsphere is

$$v_n = \frac{\hbar}{m_e r_n} \quad (11.20)$$

The allowed velocities and angular frequencies are related to  $r_n$  by

$$v_n = r_n \omega_n \quad (11.21)$$

$$\omega_n = \frac{\hbar}{m_e r_n^2} \quad (11.22)$$

20 As demonstrated in the One-Electron Atom section and by Eq. (11.22), this condition is met for the product function of a radial Dirac delta function and a time harmonic function where the angular frequency,  $\omega$ , is constant and given by Eq. (11.22).

$$\omega_n = \frac{\hbar}{m_e r_n^2} = \frac{\pi L}{A} \quad (11.23)$$

where  $L$  is the angular momentum and  $A$  is the area of the closed orbit. Consider the  
25 solution of the central force equation comprising the product of a two-dimensional ellipsoid and a time harmonic function. The spatial part of the product function is the convolution of a radial Dirac delta function with the equation of an ellipsoid. The Fourier transform of the convolution of two functions is the product of the individual Fourier transforms of the functions; thus, the boundary condition is met for an ellipsoidal-time harmonic function when

$$\omega_n = \frac{\pi \hbar}{m_e A} = \frac{\hbar}{m_e ab} \quad (11.24)$$

where the area of an ellipse is

$$A = \pi ab \quad (11.25)$$

where  $b$  and  $2b$  are the lengths of the semiminor and minor axes, respectively, and  $a$  and  $2a$  are the lengths of the semimajor and major axes, respectively. The geometry of molecular hydrogen is ellipsoidal with the internuclear axis as the principal axis; thus, the electron orbital is a two-dimensional ellipsoidal-time harmonic function. The mass follows an elliptical path, time harmonically as determined by the central field of the protons at the foci. Rotational symmetry about the internuclear axis further determines that the orbital is a prolate spheroid. In general, ellipsoidal orbits of molecular bonding, hereafter referred to as ellipsoidal molecular orbitals (MOs), have the general equation

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \quad (11.26)$$

The semiprincipal axes of the ellipsoid are  $a$ ,  $b$ ,  $c$ .

In ellipsoidal coordinates the Laplacian is

$$(\eta - \zeta)R_\xi \frac{\partial}{\partial \xi} (R_\xi \frac{\partial \phi}{\partial \xi}) + (\zeta - \xi)R_\eta \frac{\partial}{\partial \eta} (R_\eta \frac{\partial \phi}{\partial \eta}) + (\xi - \eta)R_\zeta \frac{\partial}{\partial \zeta} (R_\zeta \frac{\partial \phi}{\partial \zeta}) = 0 \quad (11.27)$$

An ellipsoidal MO is equivalent to a charged perfect conductor (i.e. no dissipation to current flow) whose surface is given by Eq. (11.26). It is a two-dimensional equipotential membrane where each MO is supported by the outward centrifugal force due to the corresponding angular velocity, which conserves its angular momentum of  $\hbar$ . It satisfies the boundary conditions for a discontinuity of charge in Maxwell's equations, Eq. (11.48). It carries a total charge  $q = -e$ , and its potential is a solution of the Laplacian in ellipsoidal coordinates, Eq. (11.27).

Excited states of orbitspheres are discussed in the Excited States of the One-Electron Atom (Quantization) section. In the case of ellipsoidal MOs, excited electronic states are created when photons of discrete frequencies are trapped in the ellipsoidal resonator cavity of the MO. The photon changes the effective charge at the MO surface where the central field is ellipsoidal and arises from the protons and the effective charge of the "trapped photon" at the foci of the MO. Force balance is achieved at a series of ellipsoidal equipotential two-dimensional surfaces confocal with the ground state ellipsoid. The "trapped photons" are solutions of the Laplacian in ellipsoidal coordinates, Eq. (11.27).

As is the case with the orbitsphere, higher and lower energy states are equally valid. The photon standing wave in both cases is a solution of the Laplacian in ellipsoidal coordinates. For an ellipsoidal resonator cavity, the relationship between an allowed circumference,  $4aE$ , and the photon standing wavelength,  $\lambda$ , is

$$5 \quad 4aE = n\lambda \quad (11.28)$$

where  $n$  is an integer and where the elliptic integral  $E$  of Eq. (11.28) is given by

$$E(k) = \int_0^{\frac{\pi}{2}} \sqrt{1 - k^2 \sin^2 \phi} d\phi \quad (11.29)$$

$$k = e = \frac{\sqrt{a^2 - b^2}}{a} \quad (11.30)$$

Applying Eqs. (11.28) and (11.29-11.30), the relationship between an allowed angular  
10 frequency given by Eq. (11.24) and the photon standing wave angular frequency,  $\omega$ , is:

$$\frac{\pi \hbar}{m_e A} = \frac{\hbar}{m_e n a_1 n b_1} = \frac{\hbar}{m_e a_n b_n} = \frac{1}{n^2} \omega_1 = \omega_n \quad (11.31)$$

where  $n = 1, 2, 3, 4, \dots$

$$n = \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \dots$$

$\omega_1$  is the allowed angular frequency for  $n = 1$

15  $a_1$  and  $b_1$  are the allowed semimajor and semiminor axes for  $n = 1$

The potential,  $\phi$ , and distribution of charge,  $\sigma$ , over the conducting surface of an ellipsoidal MO are sought given the conditions: 1.) the potential is equivalent to that of a charged ellipsoidal conductor whose surface is given by Eq. (11.26), 2.) it carries a total charge  $q = -e$ , and 3.) initially there is no external applied field. To solve this problem, a  
20 potential function must be found which satisfies Eq. (11.27), which is regular at infinity, and which is constant over the given ellipsoid. The solution is well known and is given after Stratton [2]. Consider that the Laplacian is solved in ellipsoidal coordinates wherein  $\xi$  is the parameter of a family of ellipsoids all confocal with the standard surface  $\xi = 0$  whose axes have the specified values  $a, b, c$ . The variables  $\zeta$  and  $\eta$  are the parameters of confocal  
25 hyperboloids and as such serve to measure position on any ellipsoid  $\xi = \text{constant}$ . On the surface  $\xi = 0$ ; therefore,  $\phi$  must be independent of  $\zeta$  and  $\eta$ . Due to the uniqueness property of solutions of the Laplacian, a function which satisfies Eq. (11.27), behaves

properly at infinity, and depends only on  $\xi$ , can be adjusted to represent the potential correctly at any point outside the ellipsoid  $\xi = 0$ .

Thus, it is assumed that  $\phi = \phi(\xi)$ . Then, the Laplacian reduces to

$$\frac{\partial}{\partial \xi} \left( R_\xi \frac{\partial \phi}{\partial \xi} \right) = 0 \quad R_\xi = \sqrt{(\xi + a^2)(\xi + b^2)(\xi + c^2)} \quad (11.32)$$

5 which on integration leads to

$$\phi(\xi) = C_1 \int_\xi^\infty \frac{\partial \xi}{R_\xi} \quad (11.33)$$

where  $C_1$  is an arbitrary constant. The upper limit is selected to ensure the proper behavior at infinity. When  $\xi$  becomes very large,  $R_\xi$  approaches  $\xi^{3/2}$  and

$$\phi \sim \frac{2C_1}{\sqrt{\xi}} \quad (\xi \rightarrow \infty) \quad (11.34)$$

10 Furthermore, the equation of an ellipsoid can be written in the form

$$\frac{x^2}{1 + \frac{a^2}{\xi}} + \frac{y^2}{1 + \frac{b^2}{\xi}} + \frac{z^2}{1 + \frac{c^2}{\xi}} = \xi \quad (11.35)$$

If  $r^2 = x^2 + y^2 + z^2$  is the distance from the origin to any point on the ellipsoid  $\xi$ , it is apparent that as  $\xi$  becomes very large  $\xi \rightarrow r^2$ . Thus, at great distances from the origin, the potential becomes that of a point charge at the origin:

$$15 \quad \phi \sim \frac{2C_1}{r} \quad (11.36)$$

The solution Eq. (11.33) is, therefore, regular at infinity, and the constant  $C_1$  is then determined. It has been shown by Stratton [2] that whatever the distribution, the dominant term of the expansion at remote points is the potential of a point charge at the origin equal to the total charge of the distribution—in this case  $q$ . Hence  $C_1 = \frac{q}{8\pi\epsilon_0}$ , and the potential at

20 any point is

$$\phi(\xi) = \frac{q}{8\pi\epsilon_0} \int_\xi^\infty \frac{\partial \xi}{R_\xi} \quad (11.37)$$

The equipotential surfaces are the ellipsoids  $\xi = \text{constant}$ . Eq. (11.37) is an elliptic integral and its values have been tabulated [3].

Since the distance along a curvilinear coordinate  $u^1$  is measured not by  $du^1$  but by  $h_1 du^1$ , the normal derivative in ellipsoidal coordinates is given by

$$\frac{\partial \phi}{\partial n} = \frac{1}{h_1} \frac{\partial \phi}{\partial \xi} = \frac{-q}{4\pi\epsilon_0} \frac{1}{\sqrt{(\xi-\eta)(\xi-\zeta)}} \quad (11.38)$$

where

$$5 \quad h_1 = \frac{1}{2} \frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_\xi} \quad (11.39)$$

The density of charge,  $\sigma$ , over the surface  $\xi = 0$  is

$$\sigma = \epsilon_0 \left( \frac{\partial \phi}{\partial n} \right)_{\xi=0} = \frac{q}{4\pi\sqrt{\eta\zeta}} \quad (11.40)$$

Defining  $x, y, z$  in terms of  $\xi, \eta, \zeta$ , we put  $\xi = 0$ , it may be easily verified that

$$\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4} = \frac{\zeta\eta}{a^2 b^2 c^2} \quad (\xi = 0) \quad (11.41)$$

10 Consequently, the charge density in rectangular coordinates is

$$\sigma = \frac{q}{4\pi abc} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \quad (11.42)$$

(The mass-density function of an MO is equivalent to its charge-density function where  $m$  replaces  $q$  of Eq. (11.42)). The equation of the plane tangent to the ellipsoid at the point  $x_0, y_0, z_0$  is

$$15 \quad X \frac{x_0}{a^2} + Y \frac{y_0}{b^2} + Z \frac{z_0}{c^2} = 1 \quad (11.43)$$

where  $X, Y, Z$  are running coordinates in the plane. After dividing through by the square root of the sum of the squares of the coefficients of  $X, Y$ , and  $Z$ , the right member is the distance  $D$  from the origin to the tangent plane. That is,

$$D = \frac{1}{\sqrt{\frac{x_0^2}{a^4} + \frac{y_0^2}{b^4} + \frac{z_0^2}{c^4}}} \quad (11.44)$$

20 so that for an electron MO

$$\sigma = \frac{-e}{4\pi abc} D \quad (11.45)$$

In other words, the surface density at any point on a charged ellipsoidal conductor is proportional to the perpendicular distance from the center of the ellipsoid to the plane tangent

to the ellipsoid at the point. The charge is thus greater on the more sharply rounded ends farther away from the origin.

In the case of hydrogen-type molecules and molecular ions, rotational symmetry about the internuclear axis requires that two of the axes be equal. Thus, the MO is a spheroid, and Eq. (11.37) can be integrated in terms of elementary functions. If  $a > b = c$ , the spheroid is prolate, and the potential is given by

$$\phi = \frac{1}{8\pi\epsilon_0} \frac{-e}{\sqrt{a^2 - b^2}} \ln \frac{\sqrt{\xi + a^2} + \sqrt{a^2 - b^2}}{\sqrt{\xi + a^2} - \sqrt{a^2 - b^2}} \quad (11.46)$$

## SPHEROIDAL FORCE EQUATIONS

10

### Electric Force

The spheroidal MO is a two-dimensional surface of constant potential given by Eq. (11.46) for  $\xi = 0$ . For an isolated electron MO the electric field inside is zero as given by Gauss' Law

$$\oint_S \mathbf{E} dA = \int_V \frac{\rho}{\epsilon_0} dV \quad (11.47)$$

15 where the charge density,  $\rho$ , inside the MO is zero. Gauss' Law at a two-dimensional surface with continuity of the potential across the surface according to Faraday's law in the electrostatic limit [4-6] is

$$\mathbf{n} \cdot (\mathbf{E}_1 - \mathbf{E}_2) = \frac{\sigma}{\epsilon_0} \quad (11.48)$$

$\mathbf{E}_2$  is the electric field inside which is zero. The electric field of an ellipsoidal MO with 20 semimajor and semiminor axes  $a$  and  $b = c$ , respectively, is given by substituting  $\sigma$  given by Eq. (11.38-11.42) into Eq. (11.48).

$$\mathbf{E} = \frac{\sigma}{\epsilon_0} \mathbf{i}_\xi = \frac{-e}{4\pi\epsilon_0} \frac{1}{\sqrt{(\xi - \eta)(\xi - \zeta)}} \mathbf{i}_\xi = \frac{-e}{4\pi\epsilon_0 abc} D \mathbf{i}_\xi = \frac{-e}{4\pi\epsilon_0 abc} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_\xi \quad (11.49)$$

wherein the ellipsoidal-coordinate parameter  $\xi = 0$  at the surface of the MO and  $D$  is the 25 distance from the origin to the tangent plane given by Eq. (11.44). The electric field and thus the force and potential energy between the protons and the electron MO can be solved based on three principles: (1) Maxwell's equations require that the electron MO is a equipotential energy surface that is a function of  $\xi$  alone; thus, it is a prolate spheroid, (2) stability to

radiation, and conservation first principles require that the angular velocity is constant and given in polar coordinates with respect to the origin by Eq. (11.24), and (3) the equations of motion due to the central force of each proton (Eqs. (11.5-11.19) and Eqs. (11.68-11.70)) also determine that the current is ellipsoidal, and based on symmetry, the current is a prolate spheroid. Thus, based on Maxwell's equations, conservation principles, and Newton's Laws for the equations of motion, the electron MO constraints and the motion under the force of the protons both give rise to a prolate spheroid. Since the energy of motion is determined from the Coulombic central field (Eqs. (11.5-11.19), the protons give rise to a prolate spheroidal energy surface (a surface of constant energy) that is matched to the equipotential, prolate spheroidal electron MO.

The force balance equation between the protons and the electron MO is solved to give the position of the foci, then the total energy is determined including the repulsive energy between the two protons at the foci to determine whether the original assumption of an elliptic orbit was valid. If the condition that  $E < 0$  is met, then the problem of the stable elliptic orbit is solved. In any case that this condition is not found to be met, then a stable orbit can not be formed.

The force and energy equations of a point charge(mass) (Eqs. (11.5-11.24)) are reformulated in term of densities for charge, current, mass, momentum, and potential, kinetic, and total energies. Consider an elliptical orbit shown in Figure 1 that applies to a point charge(mass) as well as a point on a continuous elliptical current loop that comprises a basis element of the continuous current density of the ellipsoidal MO. The tangent plane at any point on the ellipsoid makes equal angles with the foci radii at that point and the sum of the distance to the foci is a constant,  $2a$ . Thus, the normal is the bisector of the angle between the foci radii at that point as shown in Figure 1.

The unit vector normal to the ellipsoidal MO at a point  $(x, y, z)$  is

$$\hat{\mathbf{d}} = \frac{\left( \frac{x}{a^2}, \frac{y}{b^2}, \frac{z}{c^2} \right)}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \quad (11.50)$$

$F_1(r(t))$  and  $F_2(r(t))$  are defined as the components of the central forces centered on  $F_1$  and  $F_2$ . The components of the central forces that are normal to the ellipsoidal MO in the direction of  $\hat{\mathbf{d}}$ , the unit vector in the  $\mathbf{i}_\xi$ -direction are defined as  $F_{1\perp}(r(t))$  and  $F_{2\perp}(r(t))$ .



The normalized projections or projection factor of the sum of these central forces in the  $\hat{\mathbf{d}}$ -direction at the point  $(x, y, z)$  is

$$\begin{aligned}
 \frac{F_{1\perp}(r(t)) + F_{2\perp}(r(t))}{|F_1(r(t)) + F_2(r(t))|} &= \frac{(\mathbf{r}_1 + \mathbf{r}_2) \cdot \hat{\mathbf{d}}}{2a} \\
 &= \frac{((x-c, y, z) + (x-c, y, z)) \cdot \left(\frac{x}{a^2} + \frac{y}{b^2} + \frac{z}{b^2}\right)}{2a \sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \\
 &= \frac{\left(\frac{x^2 - cx}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{b^2}\right) + \left(\frac{x^2 + cx}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{b^2}\right)}{2a \sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \\
 &= \frac{1}{a \sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}}
 \end{aligned} \tag{11.51}$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the radial vectors of the central forces from the corresponding focus to the point  $(x, y, z)$  on the ellipsoidal MO.

The polar-coordinate elliptical orbit of a point charge due to its motion in a central inverse-squared-radius field is given by Eqs. (11.10-11.12) as the solution of the polar-coordinate-force equations, Eqs. (11.5-11.19) and (11.68-11.70). The orbit is also completely specified in Cartesian coordinates by the solution of Eqs. (11.5-11.19) and (11.68-11.70) for the semimajor and semiminor axes. Then, the corresponding polar-coordinate elliptical orbit is given as a plane cross section through the foci of the Cartesian-coordinate-system ellipsoid having the same axes given by Eq. (11.26) where  $c = b$ . Thus, the Columbic central force can be determined in terms of the general Cartesian coordinates from the polar-coordinate central force equations (Eqs. (11.5-11.19)). Consider separately the elliptical solution at each focus given in polar coordinates by Eq. (11.10):

$$r_1 = a(1-e) \frac{1+e}{1+e \cos \theta} = \frac{a(1-e^2)}{1+e \cos \theta} \tag{11.52}$$

$$r_2 = \frac{a(1-e^2)}{1+e \cos(\theta + \pi)} = \frac{a(1-e^2)}{1-e \cos \theta} \tag{11.53}$$

where

$$r_0 = a - c' = a \left(1 - \frac{c'}{a}\right) = a(1-e) \tag{11.54}$$

The magnitude of the sum of the central forces centered on  $F_1$  and  $F_2$  that are normal to the ellipsoidal MO are

$$\begin{aligned}
 |F_1(r_1)| + |F_2(r_2)| &= \frac{k}{r_1^2} + \frac{k}{r_2^2} \\
 &= k \frac{(1+e \cos \theta)^2 + (1-e \cos \theta)^2}{a^2 (1-e^2)^2} \\
 &= k \frac{1+2e \cos \theta + e^2 \cos^2 \theta + 1-2e \cos \theta + e^2 \cos^2 \theta}{a^2 (1-e^2)^2} \\
 &= k \frac{1+e^2 \cos^2 \theta + 1+e^2 \cos^2 \theta}{a^2 (1-e^2)^2} \\
 &= k \frac{2+2e^2 \cos^2 \theta}{a^2 (1-e^2)^2}
 \end{aligned} \tag{11.55}$$

The vector central forces centered on  $F_1$  and  $F_2$  that are normal to the ellipsoidal MO are then given by the product of the corresponding magnitude and vector projection given by Eqs. (11.55) and (11.51), respectively:

$$\mathbf{F}_{1\perp}(r_1) + \mathbf{F}_{2\perp}(r_2) = k \frac{2+2e^2 \cos^2 \theta}{a^2 (1-e^2)^2} \frac{1}{a \sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_\xi \tag{11.56}$$

Eq. (11.56) is based on a single point charge  $e$ . For a charge-density distribution that is given as an ellipsoidal equipotential, the  $\theta$ -dependence must vanish. In addition to the elliptical orbit being completely specified in Cartesian coordinates by the solution of Eqs. (11.5-11.19) and Eqs. (11.68-11.70) for the semimajor and semiminor axes in Eq. (11.26), the polar-coordinate elliptical orbit is also completely specified by the total constant total energy  $E$  and the angular momentum which for the electron is the constant  $\hbar$ . Considering Eq. (11.56), the corresponding total energy of the electron is conserved and is determined by the integration over the MO to give the average:

$$\mathbf{F}_{1\perp}(r_1) + \mathbf{F}_{2\perp}(r_2) = k \frac{2+e^2}{a^2 (1-e^2)^2} \frac{1}{a \sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_\xi \tag{11.57}$$

Eq. (11.57) is transformed from a two-centered-central force to a one-centered-central force to match the form of the potential of the ellipsoidal MO. In this case,

$$\mathbf{r}_1, \mathbf{r}_2 \rightarrow r(t) \mathbf{i}_\xi \tag{11.58}$$

20 In the case that

$$r_1 = r_2 = a \quad (11.59)$$

then,

$$r(t) = b \quad (11.60)$$

and the one-centered-central force is in the  $\mathbf{i}_\xi$ -direction. Thus, Eq. (11.57) transforms as

$$\begin{aligned} \mathbf{F}_{1L}(r(t)) + \mathbf{F}_{2L}(r(t)) &= k \frac{(1-e^2)^2}{b^2(2+e^2)} \frac{1}{a \sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \\ &= \frac{2+e^2}{(1-e^2)^2} k \frac{1}{ab^2 \sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_\xi \end{aligned} \quad (11.61)$$

Eq. (11.61) has the same form as that of the electric field of the ellipsoidal MO given by Eq. (11.49), except for the scaling factor of two-centered coordinates  $h_{2cc}$ :

$$h_{2cc} = \frac{2+e^2}{(1-e^2)^2} \quad (11.62)$$

As shown in the case of the derivation of the Laplacian charge-density and electric field, if  $r^2 = x^2 + y^2 + z^2$  is the distance from the origin to any point on the ellipsoid  $\xi$ , it is apparent that as  $\xi$  becomes very large  $\xi \rightarrow r^2$ . Thus, at great distances from the origin, the potential becomes that of a point charge at the origin as given by Eq. (11.36). The same boundary condition applies to the potential and field of the protons. The limiting case is also given as  $e \rightarrow 0$ . Then, to transform the scale factor to that of one-centered coordinates for an ellipsoidal MO, the reciprocal of the scaling factor multiplies the Laplacian-MO-electric-field term. The reciprocal of Eq. (11.62) is

$$h_{2cc}^{-1} = \frac{(1-e^2)^2}{2+e^2} \quad (11.63)$$

such that as  $e \rightarrow 0$ ,  $h_{2cc}^{-1} \rightarrow \frac{1}{2}$ . This transform scale factor corresponds to the interchange of the points of highest and lowest velocity on the surface and the distribution of the charge-density in the opposite manner as shown *infra*. The charge-density distribution corrects the angular variation in central force over the surface such that a solution of the central force equation of motion and the Laplacian MO are solved simultaneously. It can also be considered as a multipole normalization factor such those of the spherical harmonics and the

spherical geometric factor of atomic electrons that gives the central force as a function of  $\xi$  only.

The reciprocal of the  $h_{2cc}$  form-factor with the dependence of the charge density on the distance parameter  $r(t)$  gives

$$5 \quad \mathbf{F}_{1L}(r(t)) + \mathbf{F}_{2L}(r(t)) = k \frac{(1-e^2)^2}{b^2(2+e^2)} \frac{1}{a \sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_\xi \quad (11.64)$$

From Eq. (11.31), the magnitude of the ellipsoidal field corresponding to a below "ground state" hydrogen-type molecular ion is an integer  $p$ . The integer is one in the case of the hydrogen molecular ion and an integer greater than one in the case of each dihydrino molecular ion. The central-electric-force constant,  $k$ , from the two protons that includes the  
10 central-field contribution due photons of lower-energy states is

$$k = \frac{Ze^2}{4\pi\epsilon_0} = \frac{p2e^2}{4\pi\epsilon_0} \quad (11.65)$$

Substitution of Eq. (11.65) for  $k$  in Eq. (11.64) gives the one-center-coordinate electric force  $\mathbf{F}_{ele}$  between the protons and the ellipsoidal MO:

$$\mathbf{F}_{ele} = \mathbf{F}_{1L}(r(t)) + \mathbf{F}_{2L}(r(t)) = \frac{2pe^2}{4\pi\epsilon_0} \frac{\left(1 - \left(\frac{c'}{a}\right)^2\right)^2}{ab^2 \left(2 + \left(\frac{c'}{a}\right)^2\right)} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_\xi \quad (11.66)$$

15 where  $e$  is the charge and with the distance from the origin to a nucleus at a focus defined as  $c'$ , the eccentricity,  $e$ , is

$$e = \frac{c'}{a} \quad (11.67)$$

From the orbital equations in polar coordinates, Eqs. (11.10-11.12), the following relationship can be derived [1]:

$$20 \quad a = \frac{m \frac{L^2}{m^2}}{k(1-e^2)} \quad (11.68)$$

For any ellipse,

$$b = a\sqrt{1-e^2} \quad (11.69)$$

Thus,

$$b = a \sqrt{\frac{L^2}{m^2} \frac{m}{ka}} \quad (\text{point charge (mass) in polar coordinates}) \quad (11.70)$$

From, the equal energy condition, it can be shown that  $b$  for the motion of a point charge (mass) in polar coordinates due to a proton at one focus corresponds to

$$c' = \sqrt{a^2 - b^2} \quad (11.71)$$

5 of the MO in ellipsoidal coordinates, and  $k_1$  of one attracting focus is replaced by  $k = 2k_1$  of ellipsoidal coordinates with two attracting foci. In ellipsoidal coordinates,  $k$  is given by Eq. (11.65) and  $L$  for the electron equals  $\hbar$ .

Consider the force balance equation for the point on the ellipse at the intersection of the semiminor axis  $b$  with the ellipse. At this point called  $(0, b)$ , the distances from each  
10 focus,  $r_1$  and  $r_2$ , to the ellipse are equal. The relationship for the sum of the distances from the foci to any point on the ellipse is

$$r_1 + r_2 = 2a \quad (11.72)$$

Thus, at point  $(0, b)$ ,

$$r_1 = r_2 = a \quad (11.73)$$

15 Using Eq. (11.5), the magnitude of the force balance in the radial ( $r(t)$ ) direction, from the origin, is given by

$$mr\dot{\theta}^2 = \frac{2pe^2}{4\pi\epsilon_0 a^2} \sin\theta = \frac{2pe^2}{4\pi\epsilon_0 a^2} \frac{b}{a} \quad (11.74)$$

wherein the  $m\ddot{r}$  term is zero and  $\theta$  is the angle from the focus to point  $(0, b)$ . Using Eqs. (11.24), (11.94), and (11.95), Eq. (11.74) becomes

$$20 \quad mr\omega^2 = mb \frac{\hbar^2}{m^2 a^2 b^2} = \frac{2pe^2}{4\pi\epsilon_0 a^2} \frac{b}{a} \quad (11.75)$$

In order for the prolate spheroidal MO to be an equipotential surface, the mass and charge density must be according to Eq. (11.45). In this case, the mass and charge density along the ellipse is such that the magnitudes of the radial and transverse forces components at point  $(0, b)$  are equivalent. Furthermore, according to Eq. (11.5), the central force of each proton  
25 at a focus is separable and symmetrical to that at the other focus. Based on symmetry, the transverse forces of the two protons are in opposite directions and the radial components are in the same direction. But, the relationship between the magnitudes must still hold wherein at

point  $(0, b)$  the transverse force is equivalent to that due to the sum of the charges at one focus. The sum of the magnitudes of the transverse forces which is equivalent to a force of  $2e$  at each focus in turn is

$$|f(r)e_\theta| = \frac{2pe^2}{4\pi\epsilon_0 a^2} \cos\theta = \frac{2pe^2}{4\pi\epsilon_0 a^2} \frac{c'}{a} \quad (11.76)$$

5 Thus, using the mass and charge-density scaling factor,  $\frac{\frac{c'}{a}}{\frac{b}{a}} = \frac{c'}{b}$ , to match the equipotential

condition in Eq. (75) gives

$$b \frac{\hbar^2}{m_e \frac{c'}{b} a^2 b^2} = \frac{2 \frac{c'}{b} p e^2}{4\pi\epsilon_0 a^2} \frac{b}{a} \quad (11.77)$$

$$c'^2 = \frac{\hbar^2 4\pi\epsilon_0 a}{m_e 2 p e^2} \quad (11.78)$$

Using Eq. (1.235)

$$10 \quad c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m e^2 2 p a}} = \sqrt{\frac{a a_0}{2 p}} \quad (11.79)$$

Then, the length of the semiminor axis of the prolate spheroidal MO,  $b = c$ , is

$$b = \sqrt{a^2 - c'^2} \quad (11.80)$$

Correspondingly,  $c'$  is given by Eq. (11.71).

Substitution of Eq. (11.79) into Eq. (11.66) gives the electric force:

$$\begin{aligned}
 \mathbf{F}_{ele} &= \frac{2pe^2}{4\pi\epsilon_0} \frac{\left(1 - \left(\frac{\sqrt{aa_0}}{a}\right)^2\right)^2}{ab^2 \left(2 + \left(\frac{\sqrt{aa_0}}{a}\right)^2\right)} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_\xi \\
 &= \frac{2pe^2}{4\pi\epsilon_0} \frac{\left(1 - \frac{a_0}{2ap}\right)^2}{ab^2 \left(2 + \frac{a_0}{2ap}\right)} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_\xi \\
 &= \frac{2pe^2}{4\pi\epsilon_0} \frac{\left(1 - \frac{a_0}{2ap}\right)^2}{ab^2 \left(2 + \frac{a_0}{2ap}\right)} D \mathbf{i}_\xi
 \end{aligned} \tag{11.81}$$

### Centrifugal Force

- 5 The centrifugal force along the radial vector from each proton at each focus of the ellipsoid is given by the  $mr\dot{\theta}^2$  term of Eq. (11.5). The tangent plane at any point on the ellipsoid makes equal angles with the foci radii at that point and the sum of the distance to the foci is a constant,  $2a$ . Thus, the normal is the bisector of the angle between the foci radii at that point as shown in Figure 1. In order to satisfy the equation of motion for an equal energy surface
- 10 for both foci, the transverse component of the central force of one foci at any point on the elliptic orbit due to the central force of the other (Eq. (11.5)) must cancel on average and vice versa. Thus, the centrifugal force due to the superposition of the central forces in the direction of each foci must be normal to an ellipsoidal surface in the direction perpendicular to the direction of motion. Thus, it is in the  $\xi$ -direction. This can be only be achieved by a
- 15 time rate of change of the momentum density that compensates for the variation of the distances from each focus to each point on an elliptical cross section. Since the angular momentum must be conserved, there can be no net force in the direction transverse to the elliptical path over each orbital path. The total energy must also be conserved; thus, as shown *infra*, the distribution of the mass must also be a solution of Laplace's equation in the
- 20 parameter  $\xi$  only. Thus, the mass-density constraint is the same as the charge-density constraint. As further shown *infra*., the distribution and concomitantly the centrifugal force is

a function of  $D$ , the time-dependent distance from the center of the ellipsoid to a tangent plane given by Eq. (11.44) where  $D$  and the Cartesian coordinates are the time-dependent parameters.

Each point or coordinate position on the continuous two-dimensional electron MO defines an infinitesimal mass-density element which moves along an orbit comprising an elliptical plane cross section of the spheroidal MO through the foci. The kinetic energy of the electron is conserved. Then, the corresponding radial conservative force balance equation is

$$m(\ddot{r} + C_1 r) = 0 \quad (11.82)$$

The motion is such that eccentric angle,  $\theta$ , changes at a constant rate at each point. That is  $\theta = \omega t$  at time  $t$  where the angular velocity  $\omega$  is a constant. The solution of the homogeneous equation with  $C_1 = \omega^2$  is

$$r(t) = \mathbf{i}a \cos \omega t + \mathbf{j}b \sin \omega t \quad (11.83)$$

where  $a$  is the semimajor axis,  $b$  is semiminor axis, and the boundary conditions of  $r(t) = a$  for  $\omega t = 0$  and  $r(t) = b$  for  $\omega t = \frac{\pi}{2}$  were applied. Eq. (11.83) is the parametric equation of

the ellipse of the orbit. The velocity is given by the time derivative of the parametric position vector:

$$v(t) = \dot{r}(t) = -\mathbf{i}a\omega \sin \omega t + \mathbf{j}b\omega \cos \omega t \quad (11.84)$$

The velocity is  $\frac{\pi}{2}$  out of phase with the charge density at  $r(t) = a$  ( $\omega t = 0$ ) and  $r(t) = b$

( $\omega t = \frac{\pi}{2}$ ) such that the lowest charge density has the highest velocity and the highest charge

density has the lowest velocity. In this case, it can be shown that the current is constant along each elliptical path of the MO. Recall that nonradiation results when  $\omega = \text{constant}$  given by Eq. (11.24) that corresponds to a constant current, which further maintains the current continuity condition.

Consider Eq. (11.32) for the prolate spheroidal MO. From this equation, the mass and current-densities, the angular momentum, and the potential and kinetic energies are a function of  $\xi$  alone, and any dependence on the orthogonal coordinate parameters averages to unity. From Eq. (11.32),

$$R_\xi \frac{\partial \phi}{\partial \xi} = C_1 \quad (11.85)$$

Substitution of Eq. (11.40) into Eq. (11.85) gives



$$\int_{\xi}^{\infty} R_{\xi} h_1 \frac{e}{4\pi\sqrt{\eta\zeta}} \delta(\xi) d\xi = \varepsilon_0 C_1 = \frac{e}{8\pi} \quad (11.86)$$

where  $C_1$  is from Eq. (11.36). Substitution of Eq. (11.39) into Eq. (11.86) gives

$$\int_{\xi}^{\infty} R_{\xi} \frac{e}{4\pi\sqrt{\eta\zeta}} \frac{1}{2} \frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_{\xi}} \delta(\xi) d\xi = \frac{e}{8\pi} \quad (11.87)$$

Comparison of Eq. (11.86) with Eq. (11.87) demonstrates that the

$$5 \quad 8\pi \int_{\xi}^{\infty} R_{\xi} \frac{e}{4\pi\sqrt{\eta\zeta}} \frac{1}{2} \frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_{\xi}} \delta(\xi) d\xi = e \quad (11.88)$$

The current density  $J$  is given by the product of the constant frequency (Eq. (11.24)) and the charge density (Eq. (11.40)):

$$J = \frac{\hbar}{2\pi m_e ab} \frac{e}{4\pi\sqrt{\eta\zeta}} \quad (11.89)$$

The total constant current is dependent on  $\xi$  alone according to Eq. (11.32). Then, applying  
10 the result of Eq. (11.88) to Eq. (11.89) gives

$$\mathbf{i} = 8\pi \int_{\xi}^{\infty} R_{\xi} \frac{\hbar}{2\pi m_e ab} \frac{e}{4\pi\sqrt{\eta\zeta}} \frac{1}{2} \frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_{\xi}} \delta(\xi) d\xi \mathbf{e}_{\xi} \times \mathbf{e}_{\xi} = \frac{e\hbar}{2\pi m_e ab} \mathbf{e}_{\eta} \quad (11.90)$$

the constant current that is nonradiative.

If  $\mathbf{a}(t)$  denotes the acceleration vector, then

$$\mathbf{a}(t) = -\omega^2 \mathbf{r}(t) \mathbf{i}_r \quad (11.91)$$

15 In other words, the acceleration is centrifugal as in the case of circular motion with constant angular speed  $\omega$ . The dot product of  $\mathbf{r}(t)$  with  $\hat{\mathbf{d}}$ , the unit vector normal to the ellipsoidal MO at a point  $(x, y, z)$  given by Eq. (11.50), is

$$\mathbf{r}(t) \cdot \hat{\mathbf{d}} = \frac{(x, y, z) \cdot \left( \frac{x}{a^2}, \frac{y}{b^2}, \frac{z}{c^2} \right)}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} = \frac{\left( \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} \right)}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \quad (11.92)$$

Using Eq. (11.26), the normal component projection is

$$20 \quad \mathbf{r}(t) \cdot \hat{\mathbf{d}} = \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} = D \quad (11.93)$$

where  $D$ , the distance from the origin to the tangent plane, is given by Eq. (11.44).

The centrifugal force,  $\mathbf{F}_{cl}$ , on mass element  $m_i$  [7] given by the second term of Eq. (11.82) is

$$\mathbf{F}_{cl} = m_i a = -m_i \omega^2 r(t) \quad (11.94)$$

Substitution of the angular velocity given by Eq. (11.24) and  $m_e$  for  $m$  into Eq. (11.94) gives the centrifugal force  $\mathbf{F}_c$  on the electron that is normal to the MO surface according to Eq. (11.93):

$$\mathbf{F}_c = \frac{-\hbar^2}{m_e a^2 b^2} \mathbf{r}(t) \cdot \hat{\mathbf{d}}\mathbf{i}_\xi = \frac{-\hbar^2}{m_e a^2 b^2} D \mathbf{i}_\xi \quad (11.95)$$

$\mathbf{F}_c$  has an equivalent dependence on  $D$  as the electric force based on the charge distribution (Eq. (11.45)). This is expected based on the invariance of  $\frac{e}{m_e}$  which results in the same distribution of the mass and charge.

The equipotential charge-density distribution gives rise to the constant current condition. It also gives rise to a constant total kinetic energy condition wherein the angular velocity given by Eq. (11.24) is a constant. Recall from Eq. (11.32), that on the surface  $\xi = 0$ ;  $\phi$  must be independent of  $\zeta$  and  $\eta$  and depend only on  $\xi$  at any point outside the ellipsoid  $\xi = 0$ . Since the current and total kinetic energy are also constant on the surface  $\xi = 0$ , the total kinetic energy depends only on  $\xi$ . Thus, the centrifugal force on the mass of the electron,  $m_e$ , must be in the same direction as the electric field corresponding to  $\phi$ , normal to the electron surface wherein any tangential component in Eq. (11.94) averages to zero over the electron MO by the mass distribution given by Eqs. (11.40) and (11.45) with  $m_e$  replacing  $e$ .

The cancellation of tangential acceleration over each elliptical path maintains the charge density distribution given by Eq. (11.40) with constant current at each point on each elliptical path of the MO. Since the centrifugal force is given by Eq. (11.94), the multiplication of the mass density by the scaling factor  $h_i$  and integration with respect to  $\xi$  gives a constant net centrifugal force. Thus, the result matches those of the determination of the constant current (Eq. (11.90)) and angular momentum shown *infra*. (Eq. (11.101)) wherein the charge and mass densities given in Eqs. (11.90-11.91) and (11.100), respectively, were integrated over.

Specifically, consider the normal-directed centrifugal force,  $\mathbf{F}_{cl}$ , on mass element  $m_i$ :

$$\mathbf{F}_{ci} = -m_i \omega^2 D\mathbf{i}_\xi \quad (11.96)$$

The mass density is given by Eq. (11.40) with  $m_e$  replacing  $e$ . Then, the substitution of the mass density for  $m_i$  in Eq. (11.96) and using Eq. (11.24) for  $\omega$  gives the centrifugal force density  $\mathbf{F}_{ca}$ :

$$5 \quad \mathbf{F}_{ca} = \frac{m_e}{4\pi\sqrt{\eta\zeta}} \frac{\hbar^2}{m_e^2 a^2 b^2} D\mathbf{i}_\xi \quad (11.97)$$

Eq. (11.32) determines that the centrifugal force is a function of  $\xi$  alone, and any dependence on the transverse coordinate parameters averages to zero. Using the result of Eq. (11.88) gives the net centrifugal force  $\mathbf{F}_c$ :

$$\mathbf{F}_c = 8\pi \int_{\xi}^{\infty} \frac{1}{4\pi\sqrt{\eta\zeta}} \frac{\hbar^2}{m_e a^2 b^2} R_\xi \frac{1}{2} \frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_\xi} D\delta(\xi) d\xi \mathbf{i}_\xi = \frac{\hbar^2}{m_e a^2 b^2} D\mathbf{i}_\xi \quad (11.98)$$

10 In the limit as the ellipsoidal coordinates go over into spherical coordinates, Eq. (11.95) reduces to the centrifugal force of the spherical orbitsphere given by Eq. (1.232) with Eq. (1.47). This condition must be and is met as a further boundary condition that parallels that of Eqs. (11.32-11.37). Using the same dependence of the total mass(charge) on the scale factor  $h_i$  according to Eqs. (11.32-11.40), the further boundary conditions on the angular  
15 momentum and kinetic energy are met.

Specifically, the constant potential and current conditions and the use of Eq. (11.32) in the derivation of Eq. (11.95) also satisfy another condition, the conservation of  $\hbar$  of angular momentum of the electron. The angular momentum  $\mathbf{p}_i$  at each point  $i$  of mass  $m_i$  is

$$\begin{aligned} \mathbf{p}_i(t) &= m_i \mathbf{r}(t) \times \mathbf{v}(t) \\ &= m_i (\mathbf{i}a \cos \omega t + \mathbf{j}b \sin \omega t) \times (-\mathbf{i}a\omega \sin \omega t + \mathbf{j}b\omega \cos \omega t) \\ &= m_i ab\omega (\cos^2 \omega t + \sin^2 \omega t) \mathbf{i} \times \mathbf{j} \\ &= m_i ab\omega \mathbf{k} \end{aligned} \quad (11.99)$$

20 The mass density is given by Eq. (11.40) with  $m_e$  replacing  $e$ . Then, substitution of  $m_i$  in Eq. (11.99) by the mass density and using Eq. (11.24) for  $\omega$  gives the angular momentum density  $\mathbf{p}(t)$ :

$$\mathbf{p}(t) = ab\omega \frac{m_e}{4\pi\sqrt{\eta\zeta}} \mathbf{k} = ab \frac{\hbar}{m_e ab} \frac{m_e}{4\pi\sqrt{\eta\zeta}} \mathbf{k} \quad (11.100)$$

Using the result of Eq. (11.88) gives the total constant angular momentum  $\mathbf{L}$ :

$$\mathbf{L} = 8\pi \int_{\xi}^{\infty} \hbar \frac{1}{4\pi\sqrt{\eta\zeta}} R_{\xi} \frac{1}{2} \frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_{\xi}} \delta(\xi) d\xi \mathbf{k} = \hbar \mathbf{k} \quad (11.101)$$

Eq. (11.101) demonstrates conservation of angular momentum that is a function of  $\xi$  alone that parallels the case of atomic electrons where  $\mathbf{L}$  conservation is a function of the radius  $r$  alone as given by Eq. (1.57).

5 Similarly, the kinetic energy  $T(t)$  at each point  $i$  of mass  $m_i$  is

$$\begin{aligned} T(t) &= \frac{1}{2} m_i v(t)^2 \\ &= \frac{1}{2} m_i (-ia\omega \sin \omega t + jb\omega \cos \omega t)^2 \\ &= \frac{1}{2} m_i \omega^2 (a^2 \sin^2 \omega t + b^2 \cos^2 \omega t) \end{aligned} \quad (11.102)$$

In Eqs. (11.96-11.98),  $m_i$  was replaced by the mass density and the  $\xi$  integral was determined to give the centrifugal force in terms of the mass of the electron. The kinetic energy can also be determined from the  $\xi$  integral of the centrifugal force:

$$10 \quad T = h_{2cc} F_c \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_{\xi}} \quad (11.103)$$

The result is given in Eq. (11.119). From Eq. (11.102), the kinetic energy is time (position) dependent, but the total kinetic energy corresponding to the centrifugal force given by Eq. (11.95) satisfies the condition that the time-averaged kinetic energy is 1/2 the time-averaged potential energy for elliptic motion in an inverse-squared central force [1]. (Here, the  
15 potential and total kinetic energies are constant and correspond to the time-averaged energies of the general case.) Thus, as shown by Eqs. (11.122) (11.124), (11.262), and (11.264) energy is conserved.

### Force Balance of Hydrogen-type Molecular Ions

20 Consider the case of spheroidal coordinates based on the rotational symmetry about the semimajor axis [2]. In the limit, as the focal distance  $2c$  and the eccentricity of the series of confocal ellipses approaches zero, spheroidal coordinates go over into spherical coordinates with  $\xi \rightarrow r$  and  $\eta \rightarrow \cos \theta$ . The field of an equipotential two-dimensional charge surface of constant radius  $r = R$  is equivalent to that of a point charge of the total charge of the  
25 spherical shell at the origin. The force balance between the centrifugal force and the central Coulomb force for spherical symmetry is given by Eq. (1.232).

Similarly, the centrifugal force is the direction of  $\xi$  and balances the central Coulombic force between the protons at the foci and the electron MO. In the case of the prolate spheroidal MO, the inhomogeneous equation given by Eq. (11.5) must hold for each fixed position of  $r(t)$  since the MO is static in time due to the constant current condition.

- 5 With  $r(t)$  fixed, the  $m\ddot{r}$  term of Eq. (11.5) is zero, and the force balanced equation is the balance between the centrifugal force and the Coulombic force which are both normal to the surface of the elliptic orbit:

$$mr\dot{\theta}^2 = f(r) \quad (11.104)$$

- Substitution of Eq. (11.81) and Eq. (11.95) into Eq. (11.104) gives the force balance between  
10 the centrifugal and electric central forces:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{2pe^2}{4\pi\epsilon_0 ab^2 \left(2 + \frac{a_0}{2ap}\right)} D \quad (11.105)$$

$$\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2ap} \left(2 + \frac{a_0}{2ap}\right) = \left(1 - \frac{a_0}{2ap}\right)^2 \quad (11.106)$$

$$\frac{a_0}{ap} + \left(\frac{a_0}{2ap}\right)^2 = \left(1 - \frac{a_0}{2ap}\right)^2 \quad (11.107)$$

$$\frac{a_0}{ap} + \left(\frac{a_0}{2ap}\right)^2 = 1 - \frac{a_0}{ap} + \left(\frac{a_0}{2ap}\right)^2 \quad (11.108)$$

$$15 \quad a = 2 \frac{a_0}{p} \quad (11.109)$$

Substitution of  $a$  given by Eq. (11.109) into Eq. (11.79) gives

$$c' = \frac{a_0}{p} \quad (11.110)$$

The internuclear distance from Eq. (11.110) is

$$2c' = \frac{2a_0}{p} \quad (11.111)$$

- 20 Substitution of  $a = \frac{2a_0}{p}$  and  $c' = \frac{a_0}{p}$  into Eq. (11.80) gives the length of the semiminor axis of the prolate spheroidal MO,  $b = c$ :

$$b = \frac{\sqrt{3}}{p} a_o \quad (11.112)$$

Substitution of  $a = \frac{2a_o}{p}$  and  $c' = \frac{a_o}{p}$  into Eq. (11.67) gives the eccentricity,  $e$ :

$$e = \frac{1}{2} \quad (11.113)$$

From Eqs. (11.63-11.65), the result of Eq. (11.113) can be used to obtain the electric force

5  $\mathbf{F}_{ele}$  between the protons and the ellipsoidal MO as

$$\mathbf{F}_{ele} = Ze\mathbf{E}\mathbf{i}_\xi = h_{2cc}^{-1} \frac{p2e^2}{4\pi\epsilon_0 ab^2} D\mathbf{i}_\xi = \frac{pe^2}{8\pi\epsilon_0} D\mathbf{i}_\xi \quad (11.114)$$

where the electric field  $\mathbf{E}$  of the MO is given by Eq. (11.49). Then, the force balance of the hydrogen-type molecular ion is given by

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{pe^2}{8\pi\epsilon_0} D \quad (11.115)$$

10 which has the parametric solution given by Eq. (11.83) when

$$a = \frac{2a_o}{p} \quad (11.116)$$

The solutions for the prolate spheroidal axes and eccentricity are given by Eqs. (11.109-11.113).

## 15 ENERGIES OF HYDROGEN-TYPE MOLECULAR IONS

From Eq. (11.31), the magnitude of the ellipsoidal field corresponding to a below "ground state" hydrogen-type molecule is an integer,  $p$ . The force balance equation (Eq. (11.115)) applies for each point of the electron MO having non-constant charge (mass)-density and velocity over the equipotential and equal energy surface. The electron potential and kinetic

20 energies are thus determined from an ellipsoidal integral.

The potential energy is doubled due to the transverse electric force. The force normal to the MO is given by the dot product of the sum of the force vectors from each focus with  $\hat{\mathbf{d}}$  where the angle  $\beta$  is  $\beta = \frac{\pi}{2} - \alpha$ , and the transverse forces are given by the cross product

with  $\hat{\mathbf{d}}$ . As shown in Figure 1, equivalently, the transverse projection is given with the angle

25  $\alpha$  replacing  $\beta$  where the range of  $\alpha$  is the same as  $\beta$ . The two contributions to the

potential energy doubles it. The potential energy,  $V_e$ , of the electron MO in the field of magnitude  $p$  times that of the two protons at the foci is

$$\begin{aligned}
 V_e &= 2 \frac{-2pe^2}{4\pi\epsilon_0} D \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_{\xi}} \\
 &= \frac{-4pe^2}{8\pi\epsilon_0} \int_{\xi}^{\infty} \frac{d\xi}{(\xi+b)\sqrt{\xi+a}} \\
 &= \frac{-4pe^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \\
 &= \frac{-4pe^2}{8\pi\epsilon_0 c'} \ln \frac{a+c'}{a-c'}
 \end{aligned} \tag{11.117}$$

where

$$5 \quad \sqrt{a^2-b^2} = c' \tag{11.118}$$

$2c'$  is the distance between the foci which is the internuclear distance. The kinetic energy,  $T$ , of the electron MO follows from the same type of integral as  $V_e$  using Eqs. (7-14) of Stratton [8], Eqs. (11.37-11.46), and integral #147 of Lide [9].  $T$  is given by the corresponding integral of the centrifugal force (LHS of Eq. (11.115)) with the constraint that the current motion allows the equipotential and equal energy condition with a central field due to the protons; thus, it is corrected by the scale factor  $h_{2cc}$  given by Eq. (11.62). The  $h_{2cc}$  correction can be considered the scaling factor of the moment of inertial such that the kinetic energy is equivalent to the rotational energy for constant angular frequency  $\omega$ . The kinetic energy,  $T$ , of the electron MO is given by

$$15 \quad T = h_{2cc} \frac{-\hbar^2}{m_e a^2 b^2} D \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_{\xi}} = \frac{-4\hbar^2}{2m_e a} \int_{\xi}^{\infty} \frac{d\xi}{(\xi+b)\sqrt{\xi+a}} = \frac{-2\hbar^2}{m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{11.119}$$

The potential energy,  $V_p$ , due to proton-proton repulsion in the field of magnitude  $p$  times that of the protons at the foci ( $\xi = 0$ ) is

$$V_p = \frac{pe^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \tag{11.120}$$

20 The total energy,  $E_T$ , is given by the sum of the energy terms

$$E_T = V_e + V_p + T \tag{11.121}$$

Substitution of  $a$  and  $b$  given by Eqs. (11.109) and (11.112), respectively, into Eqs. (11.117), (11.119), (11.120), and (11.121) gives

$$V_e = \frac{-4p^2 e^2}{8\pi\epsilon_0 a_0} \ln 3 \quad (11.122)$$

$$V_p = \frac{p^2 e^2}{8\pi\epsilon_0 a_0} \quad (11.123)$$

$$T = \frac{2p^2 e^2}{8\pi\epsilon_0 a_0} \ln 3 \quad (11.124)$$

$$E_T = -13.6 \text{ eV} (4p^2 \ln 3 - p^2 - 2p^2 \ln 3) = -p^2 16.28 \text{ eV} \quad (11.125)$$

- 5 The total energy, which includes the proton-proton-repulsion term is negative which justifies the original treatment of the force balance using the analytical-mechanics equations of an ellipse that considered only the binding force between the protons and the electron and the electron centrifugal force.  $T$  is one-half the magnitude of  $V_e$  as required for an inverse-squared force [1] wherein  $V_e$  is the source of  $T$ .

10

## VIBRATION OF HYDROGEN-TYPE MOLECULAR IONS

A charge,  $q$ , oscillating according to  $\mathbf{r}_0(t) = \mathbf{d} \sin \omega_0 t$  has a Fourier spectrum

$$\mathbf{J}(\mathbf{k}, \omega) = \frac{q\omega_0 \mathbf{d}}{2} J_m(k \cos \theta d) \{ \delta[\omega - (m+1)\omega_0] + \delta[\omega - (m-1)\omega_0] \} \quad (11.126)$$

- where  $J_m$ 's are Bessel functions of order  $m$ . These Fourier components can, and do, acquire  
 15 phase velocities that are equal to the velocity of light [10]. The protons of hydrogen-type molecular ions and molecules oscillate as simple harmonic oscillators; thus, vibrating protons will radiate. Moreover, non-oscillating protons may be excited by one or more photons that are resonant with the oscillatory resonance frequency of the molecule or molecular ion, and oscillating protons may be further excited to higher energy vibrational states by resonant  
 20 photons. The energy of a photon is quantized according to Planck's equation

$$E = \hbar \omega \quad (11.127)$$

- The energy of a vibrational transition corresponds to the energy difference between the initial and final vibrational states. Each state has an electromechanical resonance frequency, and the emitted or absorbed photon is resonant with the difference in frequencies. Thus, as a general  
 25 principle, quantization of the vibrational spectrum is due to the quantized energies of photons and the electromechanical resonance of the vibrationally excited ion or molecule.



It is shown by Fowles [11] that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit. In a circular orbit in spherical coordinates, the transverse equation of motion gives

$$\dot{\theta} = \frac{L/m}{r^2} \quad (11.128)$$

5 where  $L$  is the angular momentum. The radial equation of motion is

$$m(\ddot{r} - r\dot{\theta}^2) = f(r) \quad (11.129)$$

Substitution of Eq. (11.128) into Eq. (11.129) gives

$$m\ddot{r} - \frac{m(L/m)^2}{r^3} = f(r) \quad (11.130)$$

For a circular orbit,  $r$  is a constant and  $\ddot{r} = 0$ . Thus, the radial equation of motion is given by

$$10 \quad -\frac{m(L/m)^2}{a^3} = f(a) \quad (11.131)$$

where  $a$  is the radius of the circular orbit for central force  $f(a)$  at  $r = a$ . A perturbation of the radial motion may be expressed in terms of a variable  $x$  defined by

$$x = r - a \quad (11.132)$$

The differential equation can then be written as

$$15 \quad m\ddot{x} - m(L/m)^2 (x+a)^{-3} = f(x+a) \quad (11.133)$$

Expanding the two terms involving  $x+a$  as a power series in  $x$ , gives

$$m\ddot{x} - m(L/m)^2 a^{-3} \left(1 - 3\frac{x}{a} + \dots\right) = f(a) + f'(a)x + \dots \quad (11.134)$$

Substitution of Eq. (11.131) into Eq. (11.134) and neglecting terms involving  $x^2$  and higher powers of  $x$  gives

$$20 \quad m\ddot{x} + \left[ \frac{-3}{a} f(a) - f'(a) \right] x = 0 \quad (11.135)$$

For an inverse-squared central field, the coefficient of  $x$  in Eq. (11.135) is positive, and the equation is the same as that of the simple harmonic oscillator. In this case, the particle, if perturbed, oscillates harmonically about the circle  $r = a$ , and an approximation of the angular frequency of this oscillation is

$$25 \quad \omega = \sqrt{\frac{\left[ \frac{-3}{a} f(a) - f'(a) \right]}{m}} = \sqrt{\frac{k}{m}} \quad (11.136)$$

An apsis is a point in an orbit at which the radius vector assumes an extreme value (maximum or minimum). The angle swept out by the radius vector between two consecutive apsides is called the apsidal angle. Thus, the apsidal angle is  $\pi$  for elliptical orbits under the inverse-squared law of force. In the case of a nearly circular orbit, Eq. (11.135) shows that  $r$  oscillates about the circle  $r = a$ , and the period of oscillation is given by

$$\tau_r = 2\pi \sqrt{\frac{m}{-\left[\frac{3}{a}f(a) + f'(a)\right]}} \quad (11.137)$$

The apsidal angle in this case is just the amount by which the polar angle  $\theta$  increases during the time that  $r$  oscillates from a minimum value to the succeeding maximum value which is  $\tau_r$ . From Eq. (11.128),  $\dot{\theta} = \frac{L/m}{r^2}$ ; therefore,  $\theta$  remains constant, and Eq. (11.131) gives

$$\dot{\theta} \approx \frac{L/m}{a^2} = \left[ -\frac{f(a)}{ma} \right]^{1/2} \quad (11.138)$$

Thus, the apsidal angle is given by

$$\psi = \frac{1}{2}\tau_r\dot{\theta} = \pi \left[ 3 + a \frac{f'(a)}{f(a)} \right]^{-1/2} \quad (11.139)$$

Thus, the power force of  $f(r) = -cr^n$  gives

$$\psi = \pi(3+n)^{-1/2} \quad (11.140)$$

The apsidal angle is independent of the size of the orbit in this case. The orbit is re-entrant, or repetitive, in the case of the inverse-squared law ( $n = -2$ ) for which  $\psi = \pi$ .

A prolate spheroid MO and the definition of axes are shown in Figures 5A and 5B, respectively. Consider the two nuclei A and B, each at focus of the prolate spheroid MO. From Eqs. (11.115), (11.117), and (11.119), the attractive force between the electron and each nucleus at a focus is

$$f(a) = -\frac{pe^2}{4\pi\epsilon_0 a^2} \quad (11.141)$$

and

$$f'(a) = \frac{2pe^2}{4\pi\epsilon_0 a^3} \quad (11.142)$$

In addition to the attractive force between the electron and the nuclei, there is a repulsive force between the two nuclei that is the source of a corresponding reactive force on

the reentrant electron orbit. Consider an elliptical orbital plane cross section of the MO in the xy-plane with a nucleus A at  $(-c', 0)$  and a nucleus B at  $(c', 0)$ . For B acting as the attractive focus, the reactive repulsive force at the point  $(a, 0)$ , the positive semimajor axis, depends on the distance from  $(a, 0)$  to nucleus A at  $(-c', 0)$  (i.e. the distance from the position of the  
5 electron MO at the semimajor axis to the opposite nuclear repelling center at the opposite focus). The distance is given by the sum of the semimajor axis,  $a$ , and  $c'$ , 1/2 the internuclear distance. The contribution from the repulsive force between the two protons is

$$f(a+c') = \frac{pe^2}{8\pi\epsilon_o(a+c')^2} \quad (11.143)$$

and

$$10 \quad f'(a+c') = -\frac{pe^2}{4\pi\epsilon_o(a+c')^3} \quad (11.144)$$

Thus, from Eqs. (11.136) and (11.141-11.144), the angular frequency of this oscillation is

$$\begin{aligned} \omega &= \sqrt{\frac{\frac{pe^2}{4\pi\epsilon_o a^3} - \frac{pe^2}{8\pi\epsilon_o (a+c')^3}}{\mu}} \\ &= \sqrt{\frac{\frac{pe^2}{4\pi\epsilon_o \left(\frac{2a_H}{p}\right)^3} - \frac{pe^2}{8\pi\epsilon_o \left(\frac{3a_H}{p}\right)^3}}{\mu}} \quad (11.145) \\ &= p^2 4.44865 \times 10^{14} \text{ rad/s} \end{aligned}$$

where the semimajor axis,  $a$ , is  $a = \frac{2a_H}{p}$  according to Eq. (11.116) and  $c'$  is  $c' = \frac{a_H}{p}$  according to Eq. (11.110).

15 In the case of a hydrogen molecule or molecular ion, the electrons which have a mass of 1/1836 that of the protons move essentially instantaneously, and the charge density is that of a continuous membrane. Thus, a stable electron orbit is maintained with oscillatory motion of the protons. Hydrogen molecules and molecular ions are symmetrical along the semimajor axis; thus, the oscillatory motion of protons is along this axis. Let  $x$  be the  
20 increase in the semimajor due to the reentrant orbit with a corresponding displacement of the protons along the semimajor axis from the position of the initial foci of the stationary state. The equation of proton motion due to the perturbation of an orbit having a central inverse-squared central force [1] and neglecting terms involving  $x^2$  and higher is given by

$$\mu \ddot{x} + kx = 0 \quad (11.146)$$

which has the solution in terms of the maximum amplitude of oscillation,  $A$ , the reduced nuclear mass,  $\mu$ , the restoring constant or spring constant,  $k$ , the resonance angular frequency,  $\omega_0$ , and the vibrational energy,  $E_{vib}$ , [12]

$$5 \quad A \cos \omega_0 t \quad (11.147)$$

where

$$\omega_0 = \sqrt{\frac{k}{\mu}} \quad (11.148)$$

For a symmetrical displacement  $x$ , the potential energy corresponding to the oscillation  $E_{Pvib}$  is given by

$$10 \quad E_{Pvib} = 2 \left( \frac{1}{2} kx^2 \right) = kx^2 \quad (11.149)$$

The total energy of the oscillating molecular ion,  $E_{Totalvib}$ , is given as the sum of the kinetic and potential energies

$$E_{Totalvib} = \frac{1}{2} \mu \dot{x}^2 + kx^2 \quad (11.150)$$

The velocity is zero when  $x$  is the maximum amplitude,  $A$ . The total energy of the  
15 oscillating molecular ion,  $E_{Totalvib}$ , is then given as the potential energy with  $x = A$

$$E_{Totalvib} = kA^2 \quad (11.151)$$

Thus,

$$A = \sqrt{\frac{E_{Totalvib}}{k}} \quad (11.152)$$

It is shown in the Excited States of the One-Electron Atom (Quantization) section that  
20 the change in angular frequency of the electron orbitsphere (Eq. (2.21)) is identical to the angular frequency of the photon necessary for the excitation,  $\omega_{photon}$  (Eq. (2.19)). The energy of the photon necessary to excite the equivalent transition in an electron orbitsphere is one-half of the excitation energy of the stationary cavity because the change in kinetic energy of the electron orbitsphere supplies one-half of the necessary energy. The change in the angular  
25 frequency of the orbitsphere during a transition and the angular frequency of the photon corresponding to the superposition of the free space photon and the photon corresponding to the kinetic energy change of the orbitsphere during a transition are equivalent. The correspondence principle holds. It can be demonstrated that the resonance condition between

these frequencies is to be satisfied in order to have a net change of the energy field [13]. The bound electrons are excited with the oscillating protons. Thus, the mechanical resonance frequency,  $\omega_0$ , is only one-half that of the electromechanical frequency which is equal to the frequency of the free space photon,  $\omega$ , which excites the vibrational mode of the hydrogen molecule or hydrogen molecular ion. The vibrational energy,  $E_{vib}$ , corresponding to the photon is given by

$$E_{vib} = \hbar\omega = \hbar\omega_0 = \hbar\sqrt{\frac{k}{\mu}} = 2kA^2 \quad (11.153)$$

where Planck's equation (Eq. (11.127)) was used. The reduced mass is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (11.154)$$

10 Thus,

$$A = \sqrt{\frac{\hbar\omega_0}{2k}} \quad (11.155)$$

Since the protons and electron are not fixed, but vibrate about the center of mass, the maximum amplitude is given by the reduced amplitude,  $A_{reduced}$ , given by

$$A_{reduced} = \frac{A_1 A_2}{A_1 + A_2} \quad (11.156)$$

15 where  $A_n$  is the amplitude  $n$  if the origin is fixed. Thus, Eq. (11.155) becomes

$$A_{reduced} = \frac{1}{2} \sqrt{\frac{\hbar\omega_0}{2k}} \quad (11.157)$$

and from Eq. (11.148),  $A_{reduced}$  is

$$A_{reduced} = \frac{1}{2} \sqrt{\frac{\hbar\omega_0}{2k}} = \frac{1}{2} \sqrt{\frac{\hbar}{2k}} \left( \frac{k}{\mu} \right)^{1/4} = \frac{\sqrt{\hbar}}{2^{3/2} (k\mu)^{1/4}} \quad (11.158)$$

Then, from Eq. (11.67),  $A_{c'}$ , the displacement of  $c'$  is the eccentricity  $e$  given by Eq.

20 (11.113) times  $A_{reduced}$  (Eq. (11.158)):

$$A_{c'} = eA_{reduced} = \frac{A_{reduced}}{2} = \frac{\sqrt{\hbar}}{2^{5/2} (k\mu)^{1/4}} \quad (11.159)$$

Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the

corresponding frequency,  $\omega(0)$ , for a hydrogen-type molecular ion  $H_2^+(1/p)$  given by Eqs. (11.136) and (11.145) is

$$\omega(0) = p^2 \sqrt{\frac{k(0)}{\mu}} = p^2 \sqrt{\frac{165.51 \text{ Nm}^{-1}}{\mu}} = p^2 4.449 \times 10^{14} \text{ radians/s} \quad (11.160)$$

where the reduced nuclear mass of hydrogen given by Eq. (11.154) is

$$\mu = 0.5m_p \quad (11.161)$$

and the spring constant,  $k(0)$ , given by Eqs. (11.136) and (11.145) is

$$k(0) = p^4 165.51 \text{ Nm}^{-1} \quad (11.162)$$

The transition-state vibrational energy,  $E_{vib}(0)$ , is given by Planck's equation (Eq. (11.127)):

$$E_{vib}(0) = \hbar\omega = \hbar p^2 4.44865 \times 10^{14} \text{ rad/s} = p^2 0.2928 \text{ eV} \quad (11.163)$$

10 The amplitude of the oscillation,  $A_{reduced}(0)$ , given by Eq. (11.158) and Eqs. (11.161-11.162) is

$$A_{reduced}(0) = \frac{\sqrt{\hbar}}{2^{3/2} (p^4 165.51 \text{ Nm}^{-1} \mu)^{1/4}} = \frac{5.952 \times 10^{-12} \text{ m}}{p} = 0.1125 \frac{a_o}{p} \quad (11.164)$$

Then, from Eq. (11.67),  $A_c(0)$ , the displacement of  $c'$  is the eccentricity  $e$  given by Eq. (11.113) times  $A_{reduced}(0)$  (Eq. (11.164)):

$$15 \quad A_c(0) = e A_{reduced}(0) = \frac{A_{reduced}(0)}{2} = \frac{\sqrt{\hbar}}{2^{5/2} (k\mu)^{1/4}} = \frac{0.05624 a_o}{p} \quad (11.165)$$

The spring constant and vibrational frequency for the formed molecular ion are then obtained from Eqs. (11.136) and (11.141-11.145) using the increases in the semimajor axis and internuclear distances due to vibration in the transition state. The vibrational energy,  $E_{vib}(1)$ , for the  $H_2^+(1/p)$   $\nu=1 \rightarrow \nu=0$  transition given by adding  $A_c(0)$  (Eq. (11.159)) to the  
20 distances  $a$  and  $a+c'$  in Eqs. (11.145) and (11.163) is

$$E_{vib}(1) = p^2 0.270 \text{ eV} \quad (11.166)$$

where  $\nu$  is the vibrational quantum number.

A harmonic oscillator is a linear system as given by Eq. (11.146). In this case, the predicted resonant vibrational frequencies and energies, spring constants, and amplitudes for  
25  $H_2^+(1/p)$  for vibrational transitions to higher energy  $\nu_i \rightarrow \nu_f$  are given by  $(\nu_f - \nu_i)$  times the corresponding parameters given by Eq. (11.160) and Eqs. (11.162-11.164). However,

excitation of vibration of the molecular ion by external radiation causes the semimajor axis and, consequently, the internuclear distance to increase as a function of the vibrational quantum number  $\nu$ . Consequently, the vibrational energies of hydrogen-type molecular ions are nonlinear as a function of the vibrational quantum number  $\nu$ . The lines become more  
 5 closely spaced and the change in amplitude,  $\Delta A_{reduced}$ , between successive states becomes larger as higher states are excited due to the distortion of the molecular ion in these states. The energy difference of each successive transition of the vibrational spectrum can be obtained by considering nonlinear terms corresponding to anharmonicity.

The harmonic oscillator potential energy function can be expanded about the  
 10 internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [14] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods. The energy  $\tilde{\nu}_\nu$  of state  $\nu$  is

$$\tilde{\nu}_\nu = \nu\omega_0 - \nu(\nu-1)\omega_0x_0, \quad \nu = 0, 1, 2, 3... \quad (11.167)$$

15 where

$$\omega_0x_0 = \frac{hc\omega_0^2}{4D_0} \quad (11.168)$$

$\omega_0$  is the frequency of the  $\nu=1 \rightarrow \nu=0$  transition corresponding to Eq. (11.166), and  $D_0$  is the bond dissociation energy given by Eq. (11.198). From Eqs. (11.166), (11.168), and (11.198),

$$\omega_0x_0 = \frac{100hc \left( 8.06573 \times 10^3 \frac{cm^{-1}}{eV} p^2 0.270 eV \right)^2}{4e \left( p^2 2.535 eV + p^3 0.118755 eV \right)} cm^{-1} \quad (11.169)$$

The vibrational energies of successive states are given by Eqs. (11.166-11.167) and (11.169).

Using Eqs. (11.145), (11.158-11.160), (11.162-11.169), and (11.199) the corresponding parameters for deuterium-type molecular ions with

$$\mu = m_p \quad (11.170)$$

25 are

$$\omega(0) = p^2 \sqrt{\frac{k(0)}{\mu}} = p^2 \sqrt{\frac{165.65 Nm^{-1}}{\mu}} = p^2 3.147 \times 10^{14} \text{ radians/s} \quad (11.171)$$

$$k(0) = p^4 165.65 Nm^{-1} \quad (11.172)$$

$$E_{vib}(0) = p^2 0.20714 eV \quad (11.173)$$

$$A_{\text{reduced}}(0) = \frac{\sqrt{\hbar}}{2^{3/2} (p^4 165.65 \text{ Nm}^{-1} \mu)^{1/4}} = \frac{5.004 \times 10^{-12} \text{ m}}{p} = 0.09457 \frac{a_0}{p} \quad (11.174)$$

$$E_{\text{vib}}(1) = p^2 0.193 \text{ eV} \quad (11.175)$$

$$\omega_0 x_0 = \frac{100hc \left( 8.06573 \times 10^3 \frac{\text{cm}^{-1}}{\text{eV}} p^2 0.193 \text{ eV} \right)^2}{4e(p^2 2.5770 \text{ eV} + p^3 0.118811 \text{ eV})} \text{cm}^{-1} \quad (11.176)$$

The vibrational energies of successive states are given by Eqs. (11.167) and (11.175-11.176).

5

## THE DOPPLER ENERGY TERM OF HYDROGEN-TYPE MOLECULAR IONS

As shown in the Vibration of Hydrogen-type Molecular Ions section, the electron orbiting the nuclei at the foci of an ellipse may be perturbed such that a stable reentrant orbit is  
 10 established that gives rise to a vibrational state corresponding to time harmonic oscillation of the nuclei and electron. The perturbation is caused by a photon that is resonant with the frequency of oscillation of the nuclei wherein the radiation is electric dipole with the corresponding selection rules.

Oscillation may also occur in the transition state. The perturbation arises from the  
 15 decrease in internuclear distance as the molecular bond forms. Relative to the unperturbed case given in the Force Balance of Hydrogen-type Molecular Ions section, the reentrant orbit may give rise to a decrease in the total energy while providing a transient kinetic energy to the vibrating nuclei. However, as an additional condition for stability, radiation must be considered. Regarding the potential for radiation, the nuclei may be considered point charges.  
 20 A point charge undergoing periodic motion accelerates and as a consequence radiates according to the Larmor formula (cgs units) [15]:

$$P = \frac{2e^2}{3c^3} |\dot{\mathbf{v}}|^2 \quad (11.177)$$

where  $e$  is the charge,  $\dot{\mathbf{v}}$  is its acceleration, and  $c$  is the speed of light. The radiation has a corresponding force that can be determined based on conservation of energy with radiation.

25 The radiation reaction force,  $\mathbf{F}_{\text{rad}}$ , given by Jackson [16] is

$$\mathbf{F}_{\text{rad}} = \frac{2}{3} \frac{e^2}{c^3} \ddot{\mathbf{v}} \quad (11.178)$$

Then, the Abraham-Lorentz equation of motion is given by [16]



$$m \left( \dot{\mathbf{v}} - \frac{2}{3} \frac{e^2}{mc^3} \ddot{\mathbf{v}} \right) = \mathbf{F}_{\text{ext}} \quad (11.179)$$

where  $\mathbf{F}_{\text{ext}}$  is the external force and  $m$  is the mass. The external force for the vibrating system is given by Eq. (11.146).

$$\mathbf{F}_{\text{ext}} = kx \quad (11.180)$$

5 where  $x$  is the displacement of the protons along the semimajor axis from the position of the initial foci of the stationary state in the absence of vibration with a reentrant orbit of the electron. A nonradiative state must be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied.

As shown in the Resonant Line Shape and Lamb Shift section, the spectroscopic  
10 linewidth arises from the classical rise-time band-width relationship, and the Lamb Shift is due to conservation of energy and linear momentum and arises from the radiation reaction force between the electron and the photon. The radiation reaction force in the case of the vibration of the molecular ion in the transition state corresponds to a Doppler energy,  $E_D$ , that is dependent on the motion of the electron and the nuclei. The Doppler energy of the  
15 electron is given by Eq. (2.146)

$$\bar{E}_D \cong 2\sqrt{E_K E_R} = E_{mv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} \quad (11.181)$$

where  $E_R$  is the recoil energy which arises from the photon's linear momentum given by Eq. (2.141),  $E_K$  is the vibrational kinetic energy of the reentrant orbit in the transition state, and  $M$  is the mass of the electron  $m_e$ .

20 As given in the Vibration of Hydrogen-Type Molecular Ions section, for inverse-squared central field, the coefficient of  $x$  in Eq. (11.135) is positive, and the equation is the same as that of the simple harmonic oscillator. Since the electron of the hydrogen molecular ion is perturbed as the internuclear separation decreases with bond formation, it oscillates harmonically about the semimajor axis given by Eq. (11.116), and an approximation of the  
25 angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\left[ \frac{-3}{a} f(a) - f'(a) \right]}{m_e}} = \sqrt{\frac{k}{m_e}} \quad (11.182)$$

From Eqs. (11.115), (11.117), and (11.119), the central force terms between the electron MO and the two protons are

$$f(a) = -\frac{2pe^2}{4\pi\epsilon_0 a^2} \quad (11.183)$$

and

$$f'(a) = \frac{4pe^2}{4\pi\epsilon_0 a^3} \quad (11.184)$$

Thus, the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\frac{2pe^2}{4\pi\epsilon_0 \left(\frac{2a_H}{p}\right)^3}}{m_e}} = p^2 2.06538 \times 10^{16} \text{ rad/s} \quad (11.185)$$

where the semimajor axis,  $a$ , is  $a = \frac{2a_H}{p}$  according to Eq. (11.116) including the reduced electron mass. The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar p^2 2.06538 \times 10^{16} \text{ rad/s} = p^2 13.594697 \text{ eV} \quad (11.186)$$

In Eq. (11.181), substitution of the total energy of the hydrogen molecular ion,  $E_T$ , (Eq. (11.125)) for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (11.186) for  $\bar{E}_K$  gives the Doppler energy of the electron for the reentrant orbit.

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -p^2 16.28034 \text{ eV} \sqrt{\frac{2e(p^2 13.594697 \text{ eV})}{m_e c^2}} = -p^3 0.118755 \text{ eV} \quad (11.187)$$

The total energy of the molecular ion is decreased by  $\bar{E}_D$ .

In addition to the electron, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency given in the Vibration of Hydrogen-Type Molecular Ions section. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [17]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons,  $\bar{E}_{Kvib}$ , is 1/2 of the vibrational energy of the molecular ion given by Eq. (11.166). The decrease in the energy of the hydrogen molecular ion due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electron and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  and  $\bar{E}_{Kvib}$ . Using Eq. (11.187) and  $E_{vib}$  from Eq. (11.166) gives

$$\bar{E}_{osc} = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar p^2 \sqrt{\frac{k}{\mu}} \quad (11.188)$$

$$\bar{E}_{osc} = -p^3 0.118755 \text{ eV} + \frac{1}{2} p^2 (0.29282 \text{ eV}) \quad (11.189)$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies  $\bar{E}_K$  are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies. Using Eq. (11.187) with the deuterium reduced electron mass for  $E_T$  and  $\bar{E}_D$ , and  $E_{vib}$  for  $D_2^+ (1/p)$  given by Eq. (11.173), that corresponds to the deuterium reduced nuclear mass (Eq. (11.170)), the corresponding  $\bar{E}_{osc}$  is

$$\bar{E}_{osc} = -p^3 0.118811 \text{ eV} + \frac{1}{2} p^2 (0.20714 \text{ eV}) \quad (11.190)$$

10

## TOTAL, IONIZATION, AND BOND ENERGIES OF HYDROGEN AND DEUTERIUM MOLECULAR IONS

The total energy of the hydrogen molecular ion which is equivalent to the negative of the ionization energy is given by the sum of  $E_T$  (Eqs. (11.121) and (11.125)) and  $\bar{E}_{osc}$  given by Eqs. (11.185-11.188). Thus, the total energy of the hydrogen molecular ion having a central field of  $+pe$  at each focus of the prolate spheroid molecular orbital including the Doppler term is:

$$E_T = V_e + V_p + T + \bar{E}_{osc} \quad (11.191)$$

20

$$E_T = -p^2 \left\{ \frac{e^2}{8\pi\epsilon_0 a_H} (4\ln 3 - 1 - 2\ln 3) \left[ 1 + p \sqrt{\frac{2\hbar \sqrt{\frac{2e^2}{4\pi\epsilon_0 (2a_H)^3}}}{m_e c^2}} \right] - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right\} \quad (11.192)$$

$$= -p^2 16.2803 \text{ eV} - p^3 0.118811 \text{ eV} + \frac{1}{2} p^2 \hbar \sqrt{\frac{k}{\mu}}$$

From Eqs. (11.189) and (11.191-11.192), the total energy for hydrogen-type molecular ions is

$$\begin{aligned}
E_T &= -p^2 16.28033 \text{ eV} + \bar{E}_{osc} \\
&= -p^2 16.28033 \text{ eV} - p^3 0.118755 \text{ eV} + \frac{1}{2} p^2 (0.29282 \text{ eV}) \\
&= -p^2 16.13392 \text{ eV} - p^3 0.118755 \text{ eV}
\end{aligned} \tag{11.193}$$

The total energy of the deuterium molecular ion is given by the sum of  $E_T$  (Eq. (11.125)) corrected for the reduced electron mass of  $D$  and  $\bar{E}_{osc}$  given by Eq. (11.190):

$$\begin{aligned}
E_T &= -p^2 16.284 \text{ eV} + \bar{E}_{osc} \\
&= -p^2 16.284 \text{ eV} - p^3 0.118811 \text{ eV} + \frac{1}{2} p^2 (0.20714 \text{ eV}) \\
&= -p^2 16.180 \text{ eV} - p^3 0.118811 \text{ eV}
\end{aligned} \tag{11.194}$$

- 5 The bond dissociation energy,  $E_D$ , is the difference between the total energy of the corresponding hydrogen atom or  $H(1/p)$  atom [18-19], called hydrino atom having a principal quantum number  $1/p$  where  $p$  is an integer, and  $E_T$ .

$$E_D = E(H(1/p)) - E_T \tag{11.195}$$

where [18]

$$10 \quad E(H(1/p)) = -p^2 13.59844 \text{ eV} \tag{11.196}$$

and [19]

$$E(D(1/p)) = -p^2 13.603 \text{ eV} \tag{11.197}$$

The hydrogen molecular ion bond energy,  $E_D$ , is given by Eq. (11.193) with the reduced electron mass and Eqs. (11.195-11.196):

$$\begin{aligned}
E_D &= -p^2 13.59844 - E_T \\
15 \quad &= -p^2 13.59844 - (-p^2 16.13392 \text{ eV} - p^3 0.118755 \text{ eV}) \\
&= p^2 2.535 \text{ eV} + p^3 0.118755 \text{ eV}
\end{aligned} \tag{11.198}$$

The deuterium molecular ion bond energy,  $E_D$ , is given by Eq. (11.194) with the reduced electron mass of  $D$  and Eqs. (11.195) and (11.197):

$$\begin{aligned}
E_D &= -p^2 13.603 - E_T \\
&= -p^2 13.603 - (-p^2 16.180 \text{ eV} - p^3 0.118811 \text{ eV}) \\
&= p^2 2.5770 \text{ eV} + p^3 0.118811 \text{ eV}
\end{aligned} \tag{11.199}$$

## 20 HYDROGEN-TYPE MOLECULES

## FORCE BALANCE OF HYDROGEN-TYPE MOLECULES

Hydrogen-type molecules comprise two indistinguishable electrons bound by an elliptic field. Each electron experiences a centrifugal force, and the balancing centripetal force (on each electron) is produced by the electric force between the electron and the elliptic electric field and the magnetic force between the two electrons causing the electrons to pair. In addition to nonradiation, the angular frequency given by Eq. (11.24) corresponds to a Lorentzian invariant magnetic moment of a Bohr magneton,  $\mu_B$ , as given in the Magnetic Moment of an Ellipsoidal MO section. The internal field is uniform along the major axis, and the far field is that of a dipole as shown in the Magnetic Field of an Ellipsoidal MO section. The magnetic force is derived by first determining the interaction of the two electrons due to the field of the outer electron 2 acting on the magnetic moments of electron 1 and vice versa. Insight to the behavior is given by considering the physics of a single bound electron in an externally applied uniform magnetic field as discussed in the Two-Electron Atoms section. The orbitosphere-cvf and the uniform current- (charge-) density function  $Y_0^0(\theta, \phi)$  was given in the Orbitosphere Equation of Motion for  $\ell = 0$  section and Appendix III. The resultant angular momentum projections of the spherically-symmetric orbitosphere current density,  $Y_0^0(\theta, \phi)$ , are  $L_{xy} = \frac{\hbar}{4}$  and  $L_z = \frac{\hbar}{2}$ . As shown in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magnetron section, the electron spin angular momentum gives rise to a trapped photon with  $\hbar$  of angular momentum along an S-axis. Then, the spin state of an orbitosphere comprises a photon standing wave that is phase-matched to a spherical harmonic source current, a spherical harmonic dipole  $Y_\ell^m(\theta, \phi) = \sin \theta$  with respect to the S-axis. The dipole spins about the S-axis at the angular velocity given by Eq.(1.55) with  $\hbar$  of angular momentum. S rotates about the z-axis at the Larmor frequency at  $\theta = \frac{\pi}{3}$  such that it has a static projection of the angular momentum of  $S_{\parallel} = \pm \hbar \cos \frac{\pi}{3} = \pm \frac{\hbar}{2} \mathbf{i}_{z_R}$  as given by Eq. (1.85), and from Eq. (1.84), the projection of S onto the transverse plane (xy-plane) is  $S_{\perp} = \hbar \sin \frac{\pi}{3} = \pm \sqrt{\frac{3}{4}} \hbar \mathbf{i}_{r_R}$ . Then, the vector projection of the radiation-reaction-type magnetic force of the Two Electron Atom section given by Eqs. (7.24)

and (7.31) contain the factor  $\sqrt{\frac{3}{4}}\hbar$ . This represents the maximum projection of the time-dependent magnetic moment onto an axis of the spherical-central-force system.

The orbitsphere can serve as a basis element to form a molecular orbital (MO). The total magnitude of the angular momentum of  $\hbar$  is conserved for each member of the linear combinations of  $Y_0^0(\theta, \phi)$ 's in the transition from the  $Y_0^0(\theta, \phi)$ 's to the MO. Since the charge and current densities are equivalent by the ratio of the frequency, the solution of Laplace's equation for the charge density that is an equipotential energy surface also determines the current density. The frequency and the velocity are given by Newton's laws. Specifically, the further constraint from Newton's laws that the orbital surface is a constant total energy surface and the condition of nonradiation provide that the angular velocity of each point on the surface is constant, the current is continuous and constant, and determines the corresponding velocity function. In non-spherical coordinates, the nonuniform charge distribution given by Laplace's equation is compensated by a nonuniform velocity distribution such that the constant current condition is met. Then, the conservation of the angular momentum is provided by symmetrically stretching the current density along an axis perpendicular to the plane defined by the orthogonal components of angular momentum. The angular momentum projection may be determined by first considering the case of the hydrogen molecular ion. Specifically, the angular momentum must give the results of the Stern-Gerlach experiment as shown for atomic electrons and free electrons in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section and Stern-Gerlach Experiment section, respectively.

The hydrogen-molecular-ion MO, and all MOs in general, have cylindrical symmetry along the bond axis. Thus, for the hydrogen molecular ion, the two orthogonal semiminor axes are equivalent and interchangeable. Then, in general,  $Y_0^0(\theta, \phi)$  can serve as a basis element for an MO having equal angular momentum projections along each of the semiminor axes. This defines the plane and the orthogonal axis for stretching the  $Y_0^0(\theta, \phi)$  basis element to form the MO. Thus, to conserve angular momentum,  $Y_0^0(\theta, \phi)$  is stretched along the semimajor axis as shown in Figure 2. This gives rise to an ellipsoidal surface comprised of the equivalent of elliptical-orbit, plane cross sections in the direction parallel to the semimajor axis with equal angular momentum projections along the orthogonal semiminor axes when the basis element has equal orthogonal angular momentum components.

As shown in the Exact Generation of  $Y_0^0(\theta, \phi)$  from the Orbitsphere-cvf section, the orbitsphere is comprised of the uniform function  $Y_0^0(\theta, \phi)$  corresponding to STEP ONE having the angular momentum components  $L_{xy} = 0$  and  $L_z = \frac{\hbar}{4}$  and the uniform function

$Y_0^0(\theta, \phi)$  corresponding to STEP TWO having the angular momentum components  $L_{xy} = \frac{\hbar}{4}$

5 and  $L_z = \frac{\hbar}{4}$ . These components are separable. Then, the basis element  $Y_0^0(\theta, \phi)$  for the construction of an MO that conserves the total magnitude of the angular momentum of  $\hbar$  (Eq. (1.57)) that matches the MO conditions of equal orthogonal components of angular momentum along each semiminor axis is a single  $Y_0^0(\theta, \phi)$  that is generated according to STEP TWO but with twice the angular momentum in each great-circle basis element to give

10  $L_{xy} = \frac{\hbar}{2}$  and  $L_z = \frac{\hbar}{2}$ .

Now consider the behavior of the hydrogen molecular ion in a magnetic field. As shown in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section, the photon angular momentum corresponding to the resonant excitation of the Larmor excited state is  $\hbar$ , and the angular momentum change corresponding

15 to the spin-flip transition is also  $\hbar$ . Furthermore, torque balance for the orbitsphere was determined by considering the energy minimum due to the interaction of the magnetic moments corresponding to the components of angular momentum. In the case of the hydrogen molecular ion, the Larmor-excitation photon carries  $\hbar$  of angular momentum that gives rise to a prolate spheroidal dipole current about an S-axis in the same manner as in the

20 case of the spherical dipole of the Larmor excited orbitsphere shown in Figures 1.15 and 1.16 in Chapter 1. The former are given by the prolate angular function, which comprises an associated Legendre function  $P_\ell^m(\eta)$  [20], and the latter comprises the spherical harmonic dipole  $Y_\ell^m(\theta, \phi) = \sin \theta$ . Both are with respect to the S-axis. For hydrogen molecular ion,  $\frac{\hbar}{2}$  of intrinsic spin is along each of the semiminor axes of the prolate spheroidal MO. Torque

25 balance is achieved with S along the semimajor axis as shown in Figure 3. Thus, the Larmor excitation is along the semimajor axis. In general, all bonds are cylindrically symmetrical about the internuclear or semimajor axis; thus, the Larmor precession occurs about the bond

axis of an MO wherein the intrinsic angular momentum components rotate about **S** at the Larmor frequency.

In the coordinate system rotating at the Larmor frequency (denoted by the axes labeled  $X_R$ ,  $Y_R$ , and  $Z_R$  in Figure 2), the angular momentum of **S** of magnitude  $\hbar$  is stationary. The  $Y_R$ -component of magnitude  $\frac{\hbar}{2}$  and the  $Z_R$ -component of magnitude  $\frac{\hbar}{2}$  rotate about **S** at the Larmor frequency. The rotation occurs due to a resonant excitation that results in a balance between the magnetic moment of **S** of  $\mu_B$  corresponding to its angular momentum of  $\hbar$  (Eq. (28) of Box 1.3 and Eq. (2.65)) and those of the orthogonal  $\frac{\hbar}{2}$  angular momentum components along  $Z_R$  and  $Y_R$  of  $\frac{\mu_B}{2}$ .

Then, the **S**-axis is the direction of the magnetic moment of each unpaired electron of a molecule or molecular ion. The magnetic moment of **S** of  $\mu_B$  corresponding to its  $\hbar$  of angular momentum is consistent with the Stern-Gerlach experiment wherein the Larmor excitation can only be parallel or antiparallel to the magnetic field in order to conserve the angular momentum of the electron, the photon corresponding to the Larmor excitation, and the  $\hbar$  of angular momentum of the photon that causes a 180° flip of the direction of **S**. The result is the same as that for the atomic electron and the free electron given in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section and Stern-Gerlach Experiment section, respectively. The magnetic field is given in the Magnetic Field of an Ellipsoidal Molecular Orbital section.

20

Next, consider the magnetic-pairing force of the hydrogen molecule due to the spin-angular-momentum components. The magnetic moments of electrons 1 and 2 of the hydrogen molecule cancel as they are spin paired to form an energy minimum at the radius (i.e.  $r_1 = r_2$ ). The magnetic force follows the derivation for that between the electrons of two-electron atoms as given in the Two-Electron Atoms section. The latter force was derived by first determining the interaction of the two electrons due to the field of the outer electron 2 acting on the magnetic moments of electron 1 and vice versa. It was also given by the relationship between the angular momentum, energy, and frequency for the transition of electron 2 from the continuum to the ground state. The magnitude of the magnetic force given by Eqs. (7.24) and (7.31) is equivalent to that of the centrifugal force given by Eqs.

30



(7.1-7.2) multiplied by  $\frac{1}{Z\hbar}$  times the magnitude of the photon angular momentum vector that precesses at the Larmor frequency given by Eq. (7.4). In the present case of hydrogen-type molecules, the radiation-reaction-type magnetic force arises between the electrons, each having the components shown in Figure 3. With the photon angular momentum projection of  $\hbar$  and the total nuclear (non-photon-field) of 2, the magnitude of the magnetic force between the two electrons is 1/2 that of the centrifugal force given by Eq. (11.95).

The hydrogen-type molecule is formed by the binding of an electron 2 to the hydrogen-type molecular ion comprising two protons at the foci of the prolate spheroidal MO of electron 1. The ellipsoids of electron 1 and electron 2 are confocal; thus, the electric fields and the corresponding forces are normal to the each MO of electron 1 and electron 2. The two electrons are bound by the central field of the two protons as in the case of the molecular ion. Since the field of the protons is only ellipsoidal on average, the field of the hydrogen-type molecular ion is not equivalent to an ellipsoid of charge +1 outside of the electron MO. In addition there is a spin pairing force between the two electrons. Due to the force between electron 2 and electron 1 as well as the central force of the protons, the balance between the centrifugal force and the central field of electron 2 of the hydrogen-type molecule formed by electron 2 binding to a hydrogen-type molecular ion also given by Eq. (11.115). The force balance between the centrifugal force and the sum of the Coulombic and magnetic spin-pairing forces to solve for the semimajor axis is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{pe^2}{8\pi\epsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \quad (11.200)$$

$$\frac{2a_o}{pa} - \frac{a_o}{pa} = 1 \quad (11.201)$$

$$a = \frac{a_o}{p} \quad (11.202)$$

Substitution of Eq. (11.202) into Eq. (11.79) is

$$c' = \frac{1}{p\sqrt{2}} a_o \quad (11.203)$$

The internuclear distance given by multiplying Eq. (11.203) by two is

$$2c' = \frac{a_o \sqrt{2}}{p} \quad (11.204)$$

Substitution of Eqs. (11.202-11.203) into Eq. (11.80) is

$$b = c = \frac{1}{p\sqrt{2}} a_o \quad (11.205)$$

Substitution of Eqs. (11.202-11.203) into Eq. (11.67) is

$$e = \frac{1}{\sqrt{2}} \quad (11.206)$$

For hydrogen,  $r(t) = D$  for  $\theta = n\frac{\pi}{2}$ ,  $n = 0, 1, 2, 3, 4$ . Thus, there is no dipole moment and the molecule is not predicted to be infrared active. However, it is predicted to be Raman active due to the quadrupole moment. The liquefaction temperature of  $H_2$  is also predicted to be significantly higher than isoelectronic helium.

## ENERGIES OF HYDROGEN-TYPE MOLECULES

- 10 The energy components defined previously for the molecular ion, Eqs. (11.117), (11.119), (11.120), and (11.121), apply in the case of the corresponding molecule except that all of the field lines of the protons must end on the MO comprising two-paired electrons. With spin pairing of the mirror-image-current electrons, the scaling factors due to the non-ellipsoidal variation of the electric field of the protons is unity as in the case of the sum of squares of
- 15 spherical harmonics. Thus, the hydrogen-type molecular energies are given by the integral of the forces without correction. Then, each molecular-energy component is given by the integral of corresponding force in Eq. (11.200) where each energy component is the total for the two equivalent electrons with the central-force action at the position of the electron MO where the parameters  $a$  and  $b$  are given by Eqs. (11.202) and (11.205), respectively.
- 20 The potential energy,  $V_e$ , of the two-electron MO comprising equivalent electrons in the field of magnitude  $p$  times that of the two protons at the foci is

$$\begin{aligned} V_e &= 2 \frac{-pe^2}{4\pi\epsilon_o} D \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_{\xi}} \\ &= \frac{-2pe^2}{8\pi\epsilon_o} \int_{\xi}^{\infty} \frac{d\xi}{(\xi+b)\sqrt{\xi+a}} \\ &= \frac{-2pe^2}{8\pi\epsilon_o\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \end{aligned} \quad (11.207)$$

- which is equivalent to  $Ze = 2pe$  times the potential of the MO given by Eq. (11.46) after Eq. (11.114). The potential energy,  $V_p$ , due to proton-proton repulsion in the field of magnitude
- 25  $p$  times that of the protons at the foci ( $\xi = 0$ ) is

$$V_p = \frac{p}{8\pi\epsilon_0} \frac{e^2}{\sqrt{a^2 - b^2}} \quad (11.208)$$

The kinetic energy,  $T$ , of the two-electron MO of total mass  $2m_e$  is

$$\begin{aligned} T &= 2 \frac{-\hbar^2}{2m_e a^2 b^2} D \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_{\xi}} \\ &= \frac{-\hbar^2}{2m_e a} \int_{\xi}^{\infty} \frac{d\xi}{(\xi + b)\sqrt{\xi + a}} \\ &= \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \end{aligned} \quad (11.209)$$

The magnetic energy,  $V_m$ , of the two-electron MO of total mass  $2m_e$  corresponding to the  
5 magnetic force of Eq. (11.200) is

$$\begin{aligned} V_m &= 2 \frac{-\hbar^2}{2(2m_e) a^2 b^2} D \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_{\xi}} \\ &= \frac{-\hbar^2}{4m_e a} \int_{\xi}^{\infty} \frac{d\xi}{(\xi + b)\sqrt{\xi + a}} \\ &= \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \end{aligned} \quad (11.210)$$

The total energy,  $E_T$ , is given by the sum of the energy terms (Eqs. (11.207-11.210)):

$$E_T = V_e + T + V_m + V_p \quad (11.211)$$

$$E_T = -13.60 \text{ eV} \left[ \left( 2p^2 \sqrt{2} - p^2 \sqrt{2} + \frac{p^2 \sqrt{2}}{2} \right) \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} - p^2 \sqrt{2} \right] = -p^2 31.63 \quad (11.212)$$

10 where  $a$  and  $b$  are given by Eqs. (11.202) and (11.205), respectively. The total energy, which includes the proton-proton-repulsion term is negative which justifies the original treatment of the force balance using the analytical mechanics equation of an ellipse that considered only the binding force between the protons and the electrons and the electron centrifugal force. As shown by Eqs. (11.290) and (11.292),  $T$  is one-half the magnitude of  
15  $V_e$  as required for an inverse-squared force [1] wherein  $V_e$  is the source of  $T$ .

## VIBRATION OF HYDROGEN-TYPE MOLECULES

The vibrational energy levels of hydrogen-type molecules may be solved in the same manner as hydrogen-type molecular ions given in the Vibration of Hydrogen-type Molecular Ions  
20 section. The corresponding central force terms of Eq. (11.136) are

$$f(a) = -\frac{pe^2}{8\pi\epsilon_0 a^2} \quad (11.213)$$

and

$$f'(a) = \frac{pe^2}{4\pi\epsilon_0 a^3} \quad (11.214)$$

The distance for the reactive nuclear-repulsive terms is given by the sum of the semimajor axis,  $a$ , and  $c'$ , 1/2 the internuclear distance. The contribution from the repulsive force between the two protons is

$$f(a+c') = \frac{pe^2}{8\pi\epsilon_0 (a+c')^2} \quad (11.215)$$

and

$$f'(a+c') = -\frac{pe^2}{4\pi\epsilon_0 (a+c')^3} \quad (11.216)$$

10 Thus, from Eqs. (11.136) and (11.213-11.216), the angular frequency of the oscillation is

$$\omega = \sqrt{\frac{\frac{pe^2}{8\pi\epsilon_0 a^3} - \frac{pe^2}{8\pi\epsilon_0 (a+c')^3}}{\mu}} = \sqrt{\frac{\frac{pe^2}{8\pi\epsilon_0 \left(\frac{a_0}{p}\right)^3} - \frac{pe^2}{8\pi\epsilon_0 \left(\frac{\left(1+\frac{1}{\sqrt{2}}\right)a_0}{p}\right)^3}}{\mu}} = p^2 8.62385 \times 10^{14} \text{ rad/s} \quad (11.217)$$

where the semimajor axis,  $a$ , is  $a = \frac{a_0}{p}$  according to Eq. (11.202) and  $c'$  is  $c' = \frac{a_0}{p\sqrt{2}}$

according to Eq. (11.203). Thus, during bond formation, the perturbation of the orbit  
15 determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency,  $\omega(0)$ , for a hydrogen-type molecule  $H_2(1/p)$  given by Eqs. (11.136) and (11.145) is

$$\omega(0) = p^2 \sqrt{\frac{k(0)}{\mu}} = p^2 \sqrt{\frac{621.98 \text{ Nm}^{-1}}{\mu}} = p^2 8.62385 \times 10^{14} \text{ radians/s} \quad (11.218)$$

where the reduced nuclear mass of hydrogen is given by Eq. (11.161) and the spring constant,  
20  $k(0)$ , given by Eqs. (11.136) and (11.217) is

$$k(0) = p^4 621.98 \text{ Nm}^{-1} \quad (11.219)$$

The transition-state vibrational energy,  $E_{vib}(0)$ , is given by Planck's equation (Eq. (11.127)):

$$E_{vib}(0) = \hbar\omega = \hbar p^2 8.62385 \times 10^{14} \text{ rad/s} = p^2 0.56764 \text{ eV} \quad (11.220)$$

The amplitude of oscillation,  $A_{reduced}(0)$ , given by Eqs. (11.158), (11.161), and (11.219) is

$$A_{reduced}(0) = \frac{\sqrt{\hbar}}{2^{3/2} (p^4 621.98 \text{ Nm}^{-1} \mu)^{1/4}} = \frac{4.275 \times 10^{-12} \text{ m}}{p} = 0.08079 \frac{a_o}{p} \quad (11.221)$$

Then, from Eq. (11.67),  $A_c(0)$ , the displacement of  $c'$  is the eccentricity  $e$  given by Eq.

5 (11.206) times  $A_{reduced}(0)$  (Eq. (11.221)):

$$A_c(0) = e A_{reduced}(0) = \frac{A_{reduced}(0)}{\sqrt{2}} = \frac{\sqrt{\hbar}}{4(k\mu)^{1/4}} = \frac{0.05713 a_o}{p} \quad (11.222)$$

The spring constant and vibrational frequency for the formed molecule are then obtained from Eqs. (11.136) and (11.213-11.222) using the increases in the semimajor axis and internuclear distances due to vibration in the transition state. The vibrational energy,  $E_{vib}(1)$ , for the

10  $H_2(1/p)$   $\nu=1 \rightarrow \nu=0$  transition given by adding  $A_c(0)$  (Eq. (11.222)) to the distances  $a$  and  $a+c'$  in Eqs. (11.213-11.220) is

$$E_{vib}(1) = p^2 0.517 \text{ eV} \quad (11.223)$$

where  $\nu$  is the vibrational quantum number. Using Eq. (11.176) with Eqs. (11.223) and (11.252), the anharmonic perturbation term,  $\omega_0 x_0$ , of  $H_2(1/p)$  is

$$15 \quad \omega_0 x_0 = \frac{100hc \left( 8.06573 \times 10^3 \frac{\text{cm}^{-1}}{\text{eV}} p^2 0.517 \text{ eV} \right)^2}{4e(p^2 4.151 \text{ eV} + p^3 0.326469 \text{ eV})} \text{ cm}^{-1} \quad (11.224)$$

where  $\omega_0$  is the frequency of the  $\nu=1 \rightarrow \nu=0$  transition corresponding to Eq. (11.223) and  $D_0$  is the bond dissociation energy given by Eq. (11.252). The vibrational energies of successive states are given by Eqs. (11.167) and (11.223-11.224).

Using the reduced nuclear mass given by Eq. (11.170), the corresponding parameters  
20 for deuterium-type molecules  $D_2(1/p)$  (Eqs. (11.213-11.224) and (11.253)) are

$$\omega(0) = p^2 \sqrt{\frac{k(0)}{\mu}} = p^2 \sqrt{\frac{621.98 \text{ Nm}^{-1}}{\mu}} = p^2 6.09798 \times 10^{14} \text{ radians/s} \quad (11.225)$$

$$k(0) = p^4 621.98 \text{ Nm}^{-1} \quad (11.226)$$

$$E_{vib}(0) = p^2 0.4014 \text{ eV} \quad (11.227)$$

$$A_{reduced}(0) = \frac{\sqrt{\hbar}}{2^{3/2} (p^4 621.98 \text{ Nm}^{-1} \mu)^{1/4}} = \frac{3.595 \times 10^{-12} \text{ m}}{p} = 0.06794 \frac{a_0}{p} \quad (11.228)$$

$$E_{vib}(1) = p^2 0.371 \text{ eV} \quad (11.229)$$

$$\omega_0 x_0 = \frac{100hc \left( 8.06573 \times 10^3 \frac{\text{cm}^{-1}}{\text{eV}} p^2 0.371 \text{ eV} \right)^2}{4e(p^2 4.229 \text{ eV} + p^3 0.326469 \text{ eV})} \text{cm}^{-1} \quad (11.230)$$

The vibrational energies of successive states are given by Eqs. (11.167) and (11.229-11.230).

5

## THE DOPPLER ENERGY TERM OF HYDROGEN-TYPE MOLECULES

The radiation reaction force in the case of the vibration of the molecule in the transition state also corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. Here, a nonradiative state must also be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied. Typically, a third body is required to form hydrogen-type molecules. For example, the exothermic chemical reaction of  $H + H$  to form  $H_2$  does not occur with the emission of a photon. Rather, the reaction requires a collision with a third body,  $M$ , to remove the bond energy— $H + H + M \rightarrow H_2 + M^*$  [21]. The third body distributes the energy from the exothermic reaction, and the end result is the  $H_2$  molecule and an increase in the temperature of the system. Thus, a third body removes the energy corresponding to the additional force term given by Eq. (11.180). From Eqs. (11.200), (11.207) and (11.209), the central force terms between the electron MO and the two protons are

$$f(a) = -\frac{pe^2}{4\pi\epsilon_0 a^2} \quad (11.231)$$

and

$$f'(a) = \frac{2pe^2}{4\pi\epsilon_0 a^3} \quad (11.232)$$

Thus, the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\frac{pe^2}{4\pi\epsilon_0 \left(\frac{a_0}{p}\right)^3}}{m_e}} = p^2 4.13414 \times 10^{16} \text{ rad/s} \quad (11.233)$$

where the semimajor axis,  $a$ , is  $a = \frac{a_0}{p}$  according to Eq. (11.202). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar p^2 4.13414 \times 10^{16} \text{ rad/s} = p^2 27.2116 \text{ eV} \quad (11.234)$$

In Eq. (11.181), substitution of the total energy of the hydrogen molecule,  $E_T$ , (Eq. (11.212)) for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (11.234) for  $\bar{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit.

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.635 p^2 \text{ eV} \sqrt{\frac{2e(p^2 27.216 \text{ eV})}{m_e c^2}} = -p^3 0.326469 \text{ eV} \quad (11.235)$$

The total energy of the molecule is decreased by  $\bar{E}_D$ .

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency given in the Vibration of Hydrogen-Type Molecules section. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [17]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons,  $\bar{E}_{Kvib}$ , is 1/2 of the vibrational energy of the molecule given by Eq. (11.148). The decrease in the energy of the hydrogen molecule due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  and  $\bar{E}_{Kvib}$ . Using Eq. (11.235) and  $E_{vib}$  from Eq. (11.220) gives

$$\bar{E}_{osc} = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar p^2 \sqrt{\frac{k}{\mu}} \quad (11.236)$$

$$\bar{E}_{osc} = -p^3 0.326469 \text{ eV} + \frac{1}{2} p^2 (0.56764 \text{ eV}) \quad (11.237)$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies,  $\bar{E}_K$ , are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies. Using Eq. (11.235) and  $E_{vib}$  for  $D_2(1/p)$  given by Eq. (11.227), that corresponds to the deuterium reduced nuclear mass (Eq. (11.170)), the corresponding  $\bar{E}_{osc}$  is

$$\bar{E}_{osc} = -p^3 0.326469 \text{ eV} + \frac{1}{2} p^2 (0.401380 \text{ eV}) \quad (11.238)$$

## TOTAL, IONIZATION, AND BOND ENERGIES OF HYDROGEN AND DEUTERIUM MOLECULES

The total energy of the hydrogen molecule is given by the sum of  $E_T$  (Eqs. (11.211-11.212)) and  $\bar{E}_{osc}$  given Eqs. (11.233-11.236). Thus, the total energy of the hydrogen molecule having a central field of  $+pe$  at each focus of the prolate spheroid molecular orbital including the Doppler term is

$$E_T = V_e + T + V_m + V_p + \bar{E}_{osc} \quad (11.239)$$

$$10 \quad E_T = -p^2 \left\{ \frac{e^2}{8\pi\epsilon_0 a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] \left[ 1 + p \sqrt{\frac{2\hbar \sqrt{\frac{e^2}{4\pi\epsilon_0 a_0^3}}}{m_e c^2}} \right] - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right\}$$

$$= -p^2 31.635 \text{ eV} - p^3 0.326469 \text{ eV} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (11.240)$$

From Eqs. (11.237) and (11.239-11.240), the total energy for hydrogen-type molecules is

$$\begin{aligned} E_T &= -p^2 31.635 \text{ eV} + \bar{E}_{osc} \\ &= -p^2 31.635 \text{ eV} - p^3 0.326469 \text{ eV} + \frac{1}{2} p^2 (0.56764 \text{ eV}) \\ &= -p^2 31.351 \text{ eV} - p^3 0.326469 \text{ eV} \end{aligned} \quad (11.241)$$

The total energy of the deuterium molecule is given by the sum of  $E_T$  (Eq. (11.212)) and  $\bar{E}_{osc}$  given by Eq. (11.238):

$$\begin{aligned} E_T &= -p^2 31.6354 \text{ eV} + \bar{E}_{osc} \\ &= -p^2 31.6354 \text{ eV} - p^3 0.326469 \text{ eV} + \frac{1}{2} p^2 (0.401380 \text{ eV}) \\ &= -p^2 31.4345 \text{ eV} - p^3 0.326469 \text{ eV} \end{aligned} \quad (11.242)$$

The total energy, which includes the proton-proton-repulsion term is negative which justifies the original treatment of the force balance using the analytical mechanics equation of an ellipse that considered only the binding force between the protons and the electrons, the spin-pairing force, and the electron centrifugal force.

The first ionization energy of the hydrogen molecule,  $IP_1$ ,



$$H_2(1/p) \rightarrow H_2^+(1/p) + e^- \quad (11.243)$$

is given by the difference of Eqs. (11.193) and (11.241):

$$\begin{aligned} IP_1 &= E_T(H_2^+(1/p)) - E_T(H_2(1/p)) \\ &= -p^2 16.13392 \text{ eV} - p^3 0.118755 \text{ eV} - (-p^2 31.351 \text{ eV} - p^3 0.326469 \text{ eV}) \quad (11.244) \\ &= p^2 15.2171 \text{ eV} + p^3 0.207714 \text{ eV} \end{aligned}$$

The second ionization energy,  $IP_2$ , is given by the negative of Eq. (11.193).

$$5 \quad IP_2 = p^2 16.13392 \text{ eV} + p^3 0.118755 \text{ eV} \quad (11.245)$$

The first ionization energy of the deuterium molecule,  $IP_1$ ,

$$D_2(1/p) \rightarrow D_2^+(1/p) + e^- \quad (11.246)$$

is given by the difference of Eqs. (11.194) and (11.242):

$$\begin{aligned} IP_1 &= E_T(D_2^+(1/p)) - E_T(D_2(1/p)) \\ &= -p^2 16.180 \text{ eV} - p^3 0.118811 \text{ eV} - (-p^2 31.4345 \text{ eV} - p^3 0.326469 \text{ eV}) \quad (11.247) \\ &= p^2 15.255 \text{ eV} + p^3 0.2077 \text{ eV} \end{aligned}$$

10 The second ionization energy,  $IP_2$ , is given by the negative of Eq. (11.194).

$$IP_2 = p^2 16.180 \text{ eV} + p^3 0.118811 \text{ eV} \quad (11.248)$$

The bond dissociation energy,  $E_D$ , is the difference between the total energy of the corresponding hydrogen atoms and  $E_T$

$$E_D = E(2H(1/p)) - E_T \quad (11.249)$$

15 where [18]

$$E(2H(1/p)) = -p^2 27.20 \text{ eV} \quad (11.250)$$

and [19]

$$E(2D(1/p)) = -p^2 27.206 \text{ eV} \quad (11.251)$$

The hydrogen bond energy,  $E_D$ , is given by Eqs. (11.249-11.250) and (11.241):

$$\begin{aligned} E_D &= -p^2 27.20 \text{ eV} - E_T \\ 20 \quad &= -p^2 27.20 \text{ eV} - (-p^2 31.351 \text{ eV} - p^3 0.326469 \text{ eV}) \quad (11.252) \\ &= p^2 4.151 \text{ eV} + p^3 0.326469 \text{ eV} \end{aligned}$$

The deuterium bond energy,  $E_D$ , is given by Eqs. (11.249), (11.251), and (11.242):

$$\begin{aligned}
E_D &= -p^2 27.206 \text{ eV} - E_T \\
&= -p^2 27.206 \text{ eV} - (-p^2 31.4345 \text{ eV} - p^3 0.326469 \text{ eV}) \\
&= p^2 4.229 \text{ eV} + p^3 0.326469 \text{ eV}
\end{aligned} \tag{11.253}$$

## THE HYDROGEN MOLECULAR ION $\text{H}_2[2c' = 2a_o]^+$

### 5 FORCE BALANCE OF HYDROGEN MOLECULAR ION

Force balance between the electric and centrifugal forces is given by Eq. (11.115) where  $p = 1$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_o a b^2} D \tag{11.254}$$

which has the parametric solution given by Eq. (11.83) when

$$10 \quad a = 2a_o \tag{11.255}$$

The semimajor axis,  $a$ , is also given by Eq. (11.116) where  $p = 1$ . The internuclear distance,  $2c'$ , which is the distance between the foci is given by Eq. (11.111) where  $p = 1$ .

$$2c' = 2a_o \tag{11.256}$$

The experimental internuclear distance is  $2a_o$ . The semiminor axis is given by Eq. (11.112)

15 where  $p = 1$ .

$$b = \sqrt{3}a_o \tag{11.257}$$

The eccentricity,  $e$ , is given by Eq. (11.113).

$$e = \frac{1}{2} \tag{11.258}$$

### 20 ENERGIES OF THE HYDROGEN MOLECULAR ION

The potential energy,  $V_e$ , of the electron MO in the field of the protons at the foci ( $\xi = 0$ ) is given by Eq. (11.117) where  $p = 1$

$$V_e = \frac{-4e^2}{8\pi\epsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \tag{11.259}$$

The potential energy,  $V_p$ , due to proton-proton repulsion is given by Eq. (11.120) where

25  $p = 1$

$$V_p = \frac{e^2}{8\pi\epsilon_0\sqrt{a^2 - b^2}} \quad (11.260)$$

The kinetic energy,  $T$ , of the electron MO is given by Eq. (11.119) where  $p=1$

$$T = \frac{2\hbar^2}{m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \quad (11.261)$$

Substitution of  $a$  and  $b$  given by Eqs. (11.255) and (11.257), respectively, into Eqs. (11.259-  
5 11.261) is

$$V_e = \frac{-4e^2}{8\pi\epsilon_0 a_H} \ln 3 = -59.7575 \text{ eV} \quad (11.262)$$

$$V_p = \frac{e^2}{8\pi\epsilon_0 a_H} = 13.5984 \text{ eV} \quad (11.263)$$

$$T = \frac{2e^2}{8\pi\epsilon_0 a_H} \ln 3 = 29.8787 \text{ eV} \quad (11.264)$$

The Doppler term,  $\bar{E}_{osc}$ , for hydrogen and deuterium are given by Eqs. (11.189) and (11.190),  
10 respectively, where  $p=1$

$$\bar{E}_{osc}(H_2^+) = \bar{E}_D + \bar{E}_{Kvib} = -0.118755 \text{ eV} + \frac{1}{2}(0.29282 \text{ eV}) = 0.027655 \quad (11.265)$$

$$\bar{E}_{osc}(D_2^+) = -0.118811 \text{ eV} + \frac{1}{2}(0.20714 \text{ eV}) = -0.01524 \text{ eV} \quad (11.266)$$

The total energy,  $E_T$ , for the hydrogen molecular ion given by Eqs. (11.191-11.193) is

$$\begin{aligned} E_T &= - \left\{ \frac{e^2}{8\pi\epsilon_0 a_H} (4 \ln 3 - 1 - 2 \ln 3) \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{2e^2}{4\pi\epsilon_0 (2a_H)^3}}}{m_e c^2}} \right] - \frac{1}{2} \hbar \sqrt{\frac{k}{m}} \right\} \\ &= -16.2803 \text{ eV} - 0.118811 \text{ eV} + \frac{1}{2}(0.29282 \text{ eV}) \\ &= -16.2527 \text{ eV} \end{aligned} \quad (11.267)$$

15 where in Eqs. (11.262-11.267), the radius of the hydrogen atom  $a_H$  (Eq. (1.287)) was used in place of  $a_0$  to account for the corresponding electrodynamic force between the electron and the nuclei as given in the case of the hydrogen atom by Eq. (1.231). The negative of Eq. (11.267) is the ionization energy of  $H_2^+$  and the second ionization energy,  $IP_2$ , of  $H_2$ . From

Eqs. (11.191-11.192) and (11.194), the total energy,  $E_T$ , for the deuterium molecular ion (the ionization energy of  $D_2^+$  and the second ionization energy,  $IP_2$ , of  $D_2$ ) is

$$E_T = -16.284 \text{ eV} - 0.118811 \text{ eV} + \frac{1}{2}(0.20714 \text{ eV}) = -16.299 \text{ eV} \quad (11.268)$$

The bond dissociation energy,  $E_D$ , is the difference between the total energy of the 5 corresponding hydrogen atom and  $E_T$ . The hydrogen molecular ion bond energy,  $E_D$ , including the reduced electron mass given by Eq. (11.198) where  $p = 1$  is

$$E_D = 2.535 \text{ eV} + 0.118755 \text{ eV} = 2.654 \text{ eV} \quad (11.269)$$

The experimental bond energy of the hydrogen molecular ion [22] is

$$E_D = 2.651 \text{ eV} \quad (11.270)$$

10 From Eq. (11.199) where  $p = 1$ , the deuterium molecular ion bond energy,  $E_D$ , including the reduced electron mass of  $D$  is

$$E_D = 2.5770 \text{ eV} + 0.118811 \text{ eV} = 2.6958 \text{ eV} \quad (11.271)$$

The experimental bond energy of the deuterium molecular ion [23] is

$$E_D = 2.691 \text{ eV} \quad (11.272)$$

15

## VIBRATION OF THE HYDROGEN MOLECULAR ION

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for  $H_2^+$  given by Eq. (11.160) is

$$20 \quad \omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{165.51 \text{ Nm}^{-1}}{\mu}} = 4.449 \times 10^{14} \text{ radians/s} \quad (11.273)$$

wherein  $p = 1$ . The spring constant,  $k(0)$ , for  $H_2^+$  given by Eq. (11.162) is

$$k(0) = 165.51 \text{ Nm}^{-1} \quad (11.274)$$

The vibrational energy,  $E_{vib}(0)$ , of  $H_2^+$  during bond formation given by Eq. (11.163) is

$$E_{vib}(0) = 0.29282 \text{ eV} \quad (11.275)$$

25 The amplitude of oscillation given by Eq. (11.164) is

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2} (165.51 \text{ Nm}^{-1} \mu)^{1/4}} = 5.952 \times 10^{-12} \text{ m} = 0.1125 a_0 \quad (11.276)$$

The vibrational energy for the  $H_2^+$   $\nu = 1 \rightarrow \nu = 0$  transition given by Eq. (11.166) is

$$E_{vib}(1) = 0.270 \text{ eV} \quad (11.277)$$

The experimental vibrational energy of  $H_2^+$  [14, 19] is

$$E_{vib} = 0.271 \text{ eV} \quad (11.278)$$

5 The anharmonicity term of  $H_2^+$  given by Eq. (11.169) is

$$\omega_0 x_0 = 55.39 \text{ cm}^{-1} \quad (11.279)$$

The experimental anharmonicity term of  $H_2^+$  from NIST [19] is

$$\omega_e x_e = 66.2 \text{ cm}^{-1} \quad (11.280)$$

The vibrational energy for the  $D_2^+$   $\nu = 1 \rightarrow \nu = 0$  transition given by Eq. (11.175) is

$$10 \quad E_{vib} = 0.193 \text{ eV} \quad (11.281)$$

The vibrational energy of the  $D_2^+$  [19] based on calculations from experimental data is

$$E_{vib} = 0.196 \text{ eV} \quad (11.282)$$

The anharmonicity term of  $D_2^+$  given by Eq. (11.176) is

$$\omega_0 x_0 = 27.86 \text{ cm}^{-1} \quad (11.283)$$

15 The experimental anharmonicity term of  $D_2^+$  for the state  $X^2 \sum_g^{+1} s\sigma$  is not given, but the term for state  $B^2 \sum_g^{+3} d\sigma$  from NIST [19] is

$$\omega_e x_e = 2.62 \text{ cm}^{-1} \quad (11.284)$$

## THE HYDROGEN MOLECULE $H_2$ [ $2c' = \sqrt{2}a_0$ ]

20

### FORCE BALANCE OF THE HYDROGEN MOLECULE

The force balance equation for the hydrogen molecule is given by Eq. (11.200) where  $p = 1$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \quad (11.285)$$

which has the parametric solution given by Eq. (11.83) when

$$25 \quad a = a_0 \quad (11.286)$$

The semimajor axis,  $a$ , is also given by Eq. (11.202) where  $p = 1$ . The internuclear distance,  $2c'$ , which is the distance between the foci is given by Eq. (11.204) where  $p = 1$ .

$$2c' = \sqrt{2}a_o \quad (11.287)$$

The experimental internuclear distance is  $\sqrt{2}a_o$ . The semiminor axis is given by Eq. (11.205) where  $p=1$ .

$$b = \frac{1}{\sqrt{2}}a_o \quad (11.288)$$

5 The eccentricity,  $e$ , is given by Eq. (11.206).

$$e = \frac{1}{\sqrt{2}} \quad (11.289)$$

The finite dimensions of the hydrogen molecule are evident in the plateau of the resistivity versus pressure curve of metallic hydrogen [24].

## 10 ENERGIES OF THE HYDROGEN MOLECULE

The energies of the hydrogen molecule are given by Eqs. (11.207-11.210) where  $p=1$

$$V_e = \frac{-2e^2}{8\pi\epsilon_o\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -67.8358 \text{ eV} \quad (11.290)$$

$$V_p = \frac{e^2}{8\pi\epsilon_o\sqrt{a^2-b^2}} = 19.2415 \text{ eV} \quad (11.291)$$

$$T = \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 33.9179 \text{ eV} \quad (11.292)$$

15 The energy,  $V_m$ , of the magnetic force is

$$V_m = \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.9589 \text{ eV} \quad (11.293)$$

The Doppler terms,  $\bar{E}_{osc}$ , for hydrogen and deuterium molecules are given by Eqs. (11.237) and (11.238), respectively, where  $p=1$

$$\bar{E}_{osc}(H_2) = \bar{E}_D + \bar{E}_{Kvib} = -0.326469 \text{ eV} + \frac{1}{2}(0.56764 \text{ eV}) = -0.042649 \text{ eV} \quad (11.294)$$

$$20 \quad \bar{E}_{osc}(D_2) = -0.326469 \text{ eV} + \frac{1}{2}(0.401380 \text{ eV}) = -0.125779 \text{ eV} \quad (11.295)$$

The total energy,  $E_T$ , for the hydrogen molecule given by Eqs. (11.239-11.241) is

$$\begin{aligned}
E_T &= - \left\{ \frac{e^2}{8\pi\epsilon_o a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{e^2}{4\pi\epsilon_o a_0^3}}}{m_e c^2}} \right] - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right\} \\
&= -31.635 \text{ eV} - 0.326469 \text{ eV} + \frac{1}{2} (0.56764 \text{ eV}) \\
&= -31.6776 \text{ eV}
\end{aligned} \tag{11.29}$$

6)

From Eqs. (11.239-11.240) and (11.242), the total energy,  $E_T$ , for the deuterium molecule is

$$E_T = -31.635 \text{ eV} - 0.326469 \text{ eV} + \frac{1}{2} (0.401380 \text{ eV}) = -31.7608 \text{ eV} \tag{11.297}$$

5 The first ionization energies of the hydrogen and deuterium molecules,  $IP_1$ , (Eqs. (11.243) and (11.246)) are given by the differences in the total energy of corresponding molecular ions and molecules which are given by Eqs. (11.244) and (11.247), respectively, where  $p=1$ :

$$IP_1(H_2) = 15.2171 \text{ eV} + 0.207714 \text{ eV} = 15.4248 \text{ eV} \tag{11.298}$$

$$IP_1(D_2) = 15.255 \text{ eV} + 0.2077 \text{ eV} = 15.4627 \text{ eV} \tag{11.299}$$

10 The bond dissociation energy,  $E_D$ , is the difference between the total energy of two of the corresponding hydrogen atoms and  $E_T$ . The hydrogen molecular bond energy,  $E_D$ , given by Eq. (11.252) where  $p=1$  is

$$E_D = 4.151 \text{ eV} + 0.326469 \text{ eV} = 4.478 \text{ eV} \tag{11.300}$$

The experimental bond energy of the hydrogen molecule [22] is

$$15 \quad E_D = 4.478 \text{ eV} \tag{11.301}$$

The deuterium molecular bond energy,  $E_D$ , given by Eq. (11.253) where  $p=1$  is

$$E_D = 4.229 \text{ eV} + 0.326469 \text{ eV} = 4.556 \text{ eV} \tag{11.302}$$

The experimental bond energy of the deuterium molecule [22] is

$$E_D = 4.556 \text{ eV} \tag{11.303}$$

20

## VIBRATION OF THE HYDROGEN MOLECULE

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for  $H_2$  given by Eq. (11.218) is

72

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{621.98 \text{ Nm}^{-1}}{\mu}} = 8.62385 \times 10^{14} \text{ radians / s} \quad (11.304)$$

The spring constant,  $k(0)$ , for  $H_2$  given by Eq. (11.219) is

$$k(0) = 621.98 \text{ Nm}^{-1} \quad (11.305)$$

wherein  $p = 1$ . The vibrational energy,  $E_{vib}(0)$ , of  $H_2$  during bond formation given by Eq.

5 (11.220) is

$$E_{vib}(0) = 0.56764 \text{ eV} \quad (11.306)$$

The amplitude of oscillation given by Eq. (11.221) is

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2} (p^4 621.98 \text{ Nm}^{-1} \mu)^{1/4}} = 4.275 \times 10^{-12} \text{ m} = 0.08079 a_0 \quad (11.307)$$

The vibrational energy for the  $H_2$   $\nu = 1 \rightarrow \nu = 0$  transition given by Eq. (11.223) is

$$10 \quad E_{vib}(1) = 0.517 \text{ eV} \quad (11.308)$$

The experimental vibrational energy of  $H_2$  [25-26] is

$$E_{vib}(1) = 0.5159 \text{ eV} \quad (11.309)$$

The anharmonicity term of  $H_2$  given by Eq. (11.224) is

$$\omega_0 x_0 = 120.4 \text{ cm}^{-1} \quad (11.310)$$

15 The experimental anharmonicity term of  $H_2$  from Huber and Herzberg [23] is

$$\omega_e x_e = 121.33 \text{ cm}^{-1} \quad (11.311)$$

The vibrational energy for the  $D_2$   $\nu = 1 \rightarrow \nu = 0$  transition given by Eq. (11.229) is

$$E_{vib} = 0.371 \text{ eV} \quad (11.312)$$

The experimental vibrational energy of  $D_2$  [14, 19] is

$$20 \quad E_{vib} = 0.371 \text{ eV} \quad (11.313)$$

The anharmonicity term of  $D_2$  given by Eq. (11.230) is

$$\omega_0 x_0 = 60.93 \text{ cm}^{-1} \quad (11.314)$$

The experimental anharmonicity term of  $D_2$  from NIST [19] is

$$\omega_e x_e = 61.82 \text{ cm}^{-1} \quad (11.315)$$

25 The results of the determination of the bond, vibrational, total, and ionization energies, and internuclear distances for hydrogen and deuterium molecules and molecular



ions are given in Table 11.1. The calculated results are based on first principles and given in closed form equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

Despite the predictions of standard quantum mechanics that preclude the imaging of a molecule orbital, the full three-dimensional structure of the outer molecular orbital of  $N_2$  has been recently tomographically reconstructed [27]. The charge-density surface observed is similar to that shown in Figure 5 for  $H_2$  which is direct evidence that electrons are not point-particle probability waves that have no form until they are "collapsed to a point" by measurement. Rather they are physical, two-dimensional equipotential charge density surfaces.

Table 11.1. The calculated and experimental parameters of  $H_2$ ,  $D_2$ ,  $H_2^+$  and  $D_2^+$ .

Parameter	Calculated	Experimental	Eqs.	Ref. for Exp.
$H_2$ Bond Energy	4.478 eV	4.478 eV	11.300	22
$D_2$ Bond Energy	4.556 eV	4.556 eV	11.302	22
$H_2^+$ Bond Energy	2.654 eV	2.651 eV	11.269	22
$D_2^+$ Bond Energy	2.696 eV	2.691 eV	11.271	23
$H_2$ Total Energy	31.677 eV	31.675 eV	11.296	22, 28, 18 <sup>a</sup>
$D_2$ Total Energy	31.760 eV	31.760 eV	11.297	19, 23 <sup>b</sup>
$H_2$ Ionization Energy	15.425 eV	15.426 eV	11.298	28
$D_2$ Ionization Energy	15.463 eV	15.466 eV	11.299	23
$H_2^+$ Ionization Energy	16.253 eV	16.250 eV	11.267	22, 18 <sup>c</sup>
$D_2^+$ Ionization Energy	16.299 eV	16.294 eV	11.268	19, 23 <sup>d</sup>
$H_2^+$ Magnetic Moment	$9.274 \times 10^{-24} JT^{-1}$ $\mu_B$	$9.274 \times 10^{-24} JT^{-1}$ $\mu_B$	13.1-13.7	29
Absolute $H_2$ Gas-Phase NMR Shift	-28.0 ppm	-28.0 ppm	11.411	30-31
$H_2$ Internuclear Distance <sup>e</sup>	0.748 Å $\sqrt{2}a_o$	0.741 Å	11.287	32
$D_2$ Internuclear Distance <sup>e</sup>	0.748 Å $\sqrt{2}a_o$	0.741 Å	11.287	32
$H_2^+$ Internuclear Distance <sup>f</sup>	1.058 Å $2a_o$	1.06 Å	11.256	22
$D_2^+$ Internuclear Distance <sup>e</sup>	1.058 Å $2a_o$	1.0559 Å	11.256	23
$H_2$ Vibrational Energy	0.517 eV	0.516 eV	11.308	25, 26
$D_2$ Vibrational Energy	0.371 eV	0.371 eV	11.313	14, 19
$H_2$ $\omega_e x_e$	120.4 $cm^{-1}$	121.33 $cm^{-1}$	11.310	23
$D_2$ $\omega_e x_e$	60.93 $cm^{-1}$	61.82 $cm^{-1}$	11.314	19
$H_2^+$ Vibrational Energy	0.270 eV	0.271 eV	11.277	14, 19

75

$D_2^+$ Vibrational Energy	0.193 eV	0.196 eV	11.281	19
$H_2$ J=1 to J=0	0.0148 eV	0.01509 eV	13.45	22
Rotational Energy <sup>e</sup>				
$D_2$ J=1 to J=0	0.00741 eV	0.00755 eV	13.37-13.45	22
Rotational Energy <sup>e</sup>				
$H_2^+$ J=1 to J=0	0.00740 eV	0.00739 eV	13.49	22
Rotational Energy <sup>f</sup>				
$D_2^+$ J=1 to J=0	0.00370 eV	0.003723 eV	13.37-13.43, 13.49	23
Rotational Energy <sup>e</sup>				

<sup>a</sup> The experimental total energy of the hydrogen molecule is given by adding the first (15.42593 eV) [28] and second (16.2494 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the hydrogen atom (12.59844 eV) [18] and the bond energy of  $H_2^+$  (2.651 eV) [22].

<sup>b</sup> The experimental total energy of the deuterium molecule is given by adding the first (15.466 eV) [23] and second (16.294 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the deuterium atom (12.603 eV) [19] and the bond energy of  $D_2^+$  (2.692 eV) [23].

<sup>c</sup> The experimental second ionization energy of the hydrogen molecule,  $IP_2$ , is given by the sum of the ionization energy of the hydrogen atom (12.59844 eV) [18] and the bond energy of  $H_2^+$  (2.651 eV) [22].

<sup>d</sup> The experimental second ionization energy of the deuterium molecule,  $IP_2$ , is given by the sum of the ionization energy of the deuterium atom (12.603 eV) [19] and the bond energy of  $D_2^+$  (2.692 eV) [23].

<sup>e</sup> The internuclear distances are not corrected for the reduction due to  $\bar{E}_{osc}$ .

<sup>f</sup> The internuclear distances are not corrected for the increase due to  $\bar{E}_{osc}$ .

## THE DIHYDRINO MOLECULAR ION $H_2[2c'=a_0]^+$

15

### FORCE BALANCE OF THE DIHYDRINO MOLECULAR ION

Force balance between the electric and centrifugal forces of  $H_2^+(1/2)$  is given by Eq. (11.115) where  $p = 2$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{2pe^2}{8\pi\epsilon_0 ab^2} D \quad (11.316)$$

20 which has the parametric solution given by Eq. (11.83) when

$$a = a_o \quad (11.317)$$

The semimajor axis,  $a$ , is also given by Eq. (11.116) where  $p=2$ . The internuclear distance,  $2c'$ , which is the distance between the foci is given by Eq. (11.111) where  $p=2$ .

$$2c' = a_o \quad (11.318)$$

5 The semiminor axis is given by Eq. (11.112) where  $p=2$ .

$$b = \frac{\sqrt{3}}{2} a_o \quad (11.319)$$

The eccentricity,  $e$ , is given by Eq. (11.113).

$$e = \frac{1}{2} \quad (11.320)$$

## 10 ENERGIES OF THE DIHYDRINO MOLECULAR ION

The potential energy,  $V_e$ , of the electron MO in the field of magnitude twice that of the protons at the foci ( $\xi = 0$ ) is given by Eq. (11.117) where  $p=2$

$$V_e = \frac{-8e^2}{8\pi\epsilon_o\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \quad (11.321)$$

The potential energy,  $V_p$ , due to proton-proton repulsion in the field of magnitude twice that

15 of the protons at the foci ( $\xi = 0$ ) is given by Eq. (11.120) where  $p=2$

$$V_p = \frac{2e^2}{8\pi\epsilon_o\sqrt{a^2-b^2}} \quad (11.322)$$

The kinetic energy,  $T$ , of the electron MO is given by Eq. (11.119) where  $p=2$

$$T = \frac{2\hbar^2}{m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \quad (11.323)$$

Substitution of  $a$  and  $b$  given by Eqs. (11.317) and (11.319), respectively, into Eqs. (11.321-

20 11.323) and using Eqs. (11.191-11.193) with  $p=2$  gives

$$V_e = \frac{-16e^2}{8\pi\epsilon_o a_o} \ln 3 = -239.16 \text{ eV} \quad (11.324)$$

$$V_p = \frac{4e^2}{8\pi\epsilon_o a_o} = 54.42 \text{ eV} \quad (11.325)$$

$$T = \frac{8e^2}{8\pi\epsilon_o a_o} \ln 3 = 119.58 \text{ eV} \quad (11.326)$$

$$E_T = V_e + V_p + T + \bar{E}_{osc} \quad (11.327)$$

$$E_T = -2^2 \left\{ \frac{e^2}{8\pi\epsilon_o a_H} (4\ln 3 - 1 - 2\ln 3) \left[ 1 + 2 \sqrt{\frac{2\hbar \sqrt{\frac{2e^2}{4\pi\epsilon_o (2a_H)^3}}}{m_e c^2}} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right] \right\}$$

$$= -2^2 (16.13392 \text{ eV}) - 2^3 (0.118755 \text{ eV}) \quad (11.328)$$

$$= -65.49 \text{ eV}$$

where Eqs. (11.324-11.326) are equivalent to Eqs. (11.122-11.124) with  $p = 2$ . The bond dissociation energy,  $E_D$ , given by Eq. (11.198) with  $p = 2$  is the difference between the total energy of the corresponding hydrino atom and  $E_T$  given by Eq. (11.328):

$$E_D = E_T(H(1/p)) - E_T(H_2^+(1/p))$$

$$= 2^2 (2.535 \text{ eV}) + 2^3 (0.118755 \text{ eV}) \quad (11.329)$$

$$= 11.09 \text{ eV}$$

## VIBRATION OF THE DIHYDRINO MOLECULAR ION

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for  $H_2^+(1/2)$  from Eq. (11.160) is

$$\omega(0) = 2^2 \sqrt{\frac{165.51 \text{ Nm}^{-1}}{\mu}} = 1.78 \times 10^{15} \text{ radians/s} \quad (11.330)$$

wherein  $p = 2$ . The spring constant,  $k(0)$ , for  $H_2^+(1/2)$  from Eq. (11.162) is

$$k(0) = 2^4 165.51 \text{ Nm}^{-1} = 2648 \text{ Nm}^{-1} \quad (11.331)$$

15 The amplitude of oscillation from Eq. (11.164) is

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2} (2^4 (165.51) \text{ Nm}^{-1} \mu)^{1/4}} = \frac{5.952 \times 10^{-12} \text{ m}}{2} = \frac{0.1125 a_o}{2} \quad (11.332)$$

The vibrational energy,  $E_{vib}(1)$ , for the  $\nu = 1 \rightarrow \nu = 0$  transition given by Eq. (11.166) is

$$E_{vib}(1) = 2^2 (0.270 \text{ eV}) = 1.08 \text{ eV} \quad (11.333)$$

# THE DIHYDRINO MOLECULE $H_2 \left[ 2c' = \frac{a_o}{\sqrt{2}} \right]$

## FORCE BALANCE OF THE DIHYDRINO MOLECULE

The force balance equation for the dihydrino molecule  $H_2(1/2)$  is given by Eq. (11.200)

5 where  $p = 2$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{2e^2}{8\pi\epsilon_o a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \quad (11.334)$$

which has the parametric solution given by Eq. (11.83) when

$$a = \frac{a_o}{2} \quad (11.335)$$

The semimajor axis,  $a$ , is also given by Eq. (11.202) where  $p = 2$ . The internuclear

10 distance,  $2c'$ , which is the distance between the foci is given by Eq. (11.204) where  $p = 2$ .

$$2c' = \frac{1}{\sqrt{2}} a_o \quad (11.336)$$

The semiminor axis is given by Eq. (11.205) where  $p = 2$ .

$$b = c = \frac{1}{2\sqrt{2}} a_o \quad (11.337)$$

The eccentricity,  $e$ , is given by Eq. (11.206).

$$15 \quad e = \frac{1}{\sqrt{2}} \quad (11.338)$$

## ENERGIES OF THE DIHYDRINO MOLECULE

The energies of the dihydrino molecule  $H_2(1/2)$  are given by Eqs. (11.207-11.210) and Eqs.

(11.239-11.241) with  $p = 2$

$$20 \quad V_e = \frac{-4e^2}{8\pi\epsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -271.34 \text{ eV} \quad (11.339)$$

$$V_p = \frac{2}{8\pi\epsilon_o} \frac{e^2}{\sqrt{a^2 - b^2}} = 76.97 \text{ eV} \quad (11.340)$$

$$T = \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 135.67 \text{ eV} \quad (11.341)$$

The energy,  $V_m$ , of the magnetic force is

$$V_m = \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -67.84 \text{ eV} \quad (11.342)$$

$$E_T = V_e + T + V_m + V_p + \bar{E}_{osc} \quad (11.343)$$

$$E_T = -2^2 \left\{ \frac{e^2}{8\pi\epsilon_0 a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] \left[ 1 + 2 \sqrt{\frac{2\hbar \sqrt{\frac{e^2}{4\pi\epsilon_0 a_0^3}}}{m_e c^2}} \right] - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right\}$$

$$= -2^2 (31.351 \text{ eV}) - 2^3 (0.326469 \text{ eV}) \quad (11.344)$$

$$= -128.02 \text{ eV}$$

where Eqs. (11.339-11.342) are equivalent to Eqs. (11.207-11.210) with  $p = 2$ . The bond dissociation energy,  $E_D$ , given by Eq. (11.252) with  $p = 2$  is the difference between the total energy of the corresponding hydrino atoms and  $E_T$  given by Eq. (11.344).

$$E_D = E_T(2H(1/p)) - E_T(H_2(1/p))$$

$$= 2^2 (4.151 \text{ eV}) + 2^3 (0.326469 \text{ eV}) \quad (11.345)$$

$$= 19.22 \text{ eV}$$

## VIBRATION OF THE DIHYDRINO MOLECULE

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for the  $H_2(1/2)$  from Eq. (11.217) is

$$\omega(0) = 2^2 \sqrt{\frac{k}{\mu}} = 2^2 \sqrt{\frac{621.98 \text{ Nm}^{-1}}{\mu}} = 3.45 \times 10^{15} \text{ radians/s} \quad (11.346)$$

wherein  $p = 2$ . The spring constant,  $k(0)$ , for  $H_2(1/2)$  from Eq. (11.219) is

$$k(0) = 2^4 621.98 \text{ Nm}^{-1} = 9952 \text{ Nm}^{-1} \quad (11.347)$$

The amplitude of oscillation from Eq. (11.221) is

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2} (2^4 (621.98) \text{ Nm}^{-1} \mu)^{1/4}} = \frac{4.275 \times 10^{-12} \text{ m}}{2} = \frac{0.08079 a_0}{2} \quad (11.348)$$

The vibrational energy,  $E_{vib}(1)$ , of  $H_2(1/2)$  from Eq. (11.223) is

$$E_{vib}(1) = 2^2 (0.517) \text{ eV} = 2.07 \text{ eV} \quad (11.349)$$

## GEOMETRY

The internuclear distance can also be determined geometrically. The spheroidal MO of the hydrogen molecule is an equipotential energy surface, which is an energy minimum surface.

For the hydrogen molecule, the electric field is zero for  $\xi > 0$ . Consider two hydrogen atoms

5 A and B approaching each other. Consider that the two electrons form a spheroidal MO as the two atoms overlap, and the charge is distributed such that an equipotential two-dimensional surface is formed. The electric fields of atoms A and B add vectorially as the atoms overlap. The energy at the point of intersection of the overlapping orbitspheres decreases to a minimum as they superimpose and then rises with further overlap. When this  
10 energy is a minimum the internuclear distance is determined. It can be demonstrated [33] that when two hydrogen orbitspheres superimpose such that the radial electric field vector from nucleus A and B makes a  $45^\circ$  angle with the point of intersection of the two original orbitspheres, the electric energy of interaction between orbitspheres given by

$$E_{\text{interaction}} = 2 \times \frac{1}{2} \epsilon_o \int \Delta E^2 dv \quad (11.350)$$

15 is a minimum (Figure 7.1 of [33]). The MO is a minimum potential energy surface; therefore, a minimum of energy of one point on the surface is a minimum for the entire surface of the MO. Thus,

$$R_{H_2} = \sqrt{2} a_o = 0.748 \text{ \AA} \quad (11.351)$$

The experimental internuclear bond distance is  $0.746 \text{ \AA}$ .

20

## DIHYDRINO IONIZATION ENERGIES

The first ionization energy,  $IP_1$ , of the dihydrino molecule



is given by Eq. (11.244) with  $p = 2$ .

$$25 \quad IP_1 = E_T(H_2^+(1/p)) - E_T(H_2(1/p)) \quad (11.353)$$

$$IP_1 = 2^2 (15.2171 \text{ eV}) + 2^3 (0.2077 \text{ eV}) = 62.53 \text{ eV} \quad (11.354)$$

The second ionization energy,  $IP_2$ , is given by Eq. (11.245) with  $p = 2$ .

$$IP_2 = 2^2 (16.13392 \text{ eV}) + 2^3 (0.118755 \text{ eV}) = 65.49 \text{ eV} \quad (11.355)$$

A hydrino atom can react with a hydrogen, deuterium, or tritium nucleus to form a  
30 dihydrino molecular ion that further reacts with an electron to form a dihydrino molecule.





The energy released is

$$E = E(H(1/p)) - E_T \quad (11.357)$$

where  $E_T$  is given by Eq. (11.241).

- 5 A hydrino atom can react with a hydrogen, deuterium, or tritium atom to form a dihydrino molecule.



The energy released is

$$E = E(H(1/p)) + E(H) - E_T \quad (11.359)$$

- 10 where  $E_T$  is given by Eq. (11.241).

## SIZES OF REPRESENTATIVE ATOMS AND MOLECULES

### ATOMS

15

#### Helium Atom (He)

Helium comprises the nucleus at the origin and two electrons as a spherical shell at  $r = 0.567a_0$ .

#### 20 Hydrogen Atom ( $H[a_H]$ )

Hydrogen comprises the nucleus at the origin and the electron as a spherical shell at  $r = a_H$ .

#### Hydrino Atom ( $H\left[\frac{a_H}{2}\right]$ )

Hydrino atom (1/2) comprises the nucleus at the origin and the electron as a spherical shell at

$$25 \quad r = \frac{a_H}{2}.$$

### MOLECULES

#### Hydrogen Molecular Ion ( $H_2[2c' = 2a_0]^+$ )

$$a = 2a_0$$

$$b = c = \sqrt{3}a_0$$

$$c' = a_0$$

$$2c' = 2a_0$$

5 Hydrogen Molecule ( $\text{H}_2 [2\mathbf{c}' = \sqrt{2}\mathbf{a}_0]$ )

$$a = a_0$$

$$b = c = \frac{1}{\sqrt{2}}a_0$$

$$c' = \frac{1}{\sqrt{2}}a_0$$

$$2c' = \sqrt{2}a_0$$

10

Dihydrino Molecular Ion ( $\text{H}_2 [2\mathbf{c}' = \mathbf{a}_0]^+$ )

$$a = a_0$$

$$b = c = \frac{\sqrt{3}}{2}a_0$$

$$b = c = \frac{1}{2}a_0$$

15  $2c' = a_0$

Dihydrino Molecule ( $\text{H}_2 \left[ 2\mathbf{c}' = \frac{1}{\sqrt{2}}\mathbf{a}_0 \right]$ )

$$a = \frac{1}{2}a_0$$

$$b = c = \frac{1}{2\sqrt{2}}a_0$$

20  $c' = \frac{1}{2\sqrt{2}}a_0$

$$2c' = \frac{1}{\sqrt{2}}a_0$$

## ORTHO-PARA TRANSITION OF HYDROGEN-TYPE MOLECULES

Each proton of hydrogen-type molecules possesses a magnetic moment, which is derived in the Proton and Neutron section and is given by

$$\mu_p = \frac{\left(\frac{2}{3}\right)^2 e\hbar}{2 \frac{m_p}{2\pi}} \quad (11.360)$$

- 5 The magnetic moment,  $\mathbf{m}$ , of the proton is given by Eq. (11.360), and the magnetic field of the proton follows from the relationship between the magnetic dipole field and the magnetic moment,  $\mathbf{m}$ , as given by Jackson [34] where  $\mathbf{m} = \mu_p \mathbf{i}_z$ .

$$\mathbf{H} = \frac{\mu_p}{r^3} (\mathbf{i}_r 2 \cos \theta - \mathbf{i}_\theta \sin \theta) \quad (11.361)$$

Multiplication of Eq. (11.361) by the permeability of free space,  $\mu_0$ , gives the magnetic flux,

- 10  $\mathbf{B}$ , due to proton one at proton two.

$$\mathbf{B} = \frac{\mu_0 \mu_p}{r^3} (\mathbf{i}_r 2 \cos \theta - \mathbf{i}_\theta \sin \theta) \quad (11.362)$$

$\Delta E_{mag}^{\text{ortho/para}}$ , the energy to flip the orientation of proton two's magnetic moments,  $\mu_p$ , from ortho (parallel magnetic moments) to para (antiparallel magnetic moments) with respect to the direction of the magnetic moment of proton one with corresponding magnetic flux  $\mathbf{B}$  is

$$15 \quad \Delta E_{mag}^{\text{ortho/para}} = -2\mu_p \mathbf{B} = \frac{-2\mu_0 \mu_p^2}{r^3} \quad (11.363)$$

where  $r$  is the internuclear distance  $2c'$  where  $c'$  is given by Eq. (11.204). Substitution of the internuclear distance into Eq. (11.363) for  $r$  gives

$$\Delta E_{mag}^{\text{ortho/para}} = -2\mu_p \mathbf{B} = \frac{-2\mu_0 \mu_p^2 p^3}{(\sqrt{2}a_o)^3} \quad (11.364)$$

The frequency,  $f$ , can be determined from the energy using the Planck relationship, Eq.

- 20 (2.18).

$$f = \frac{\Delta E_{mag}^{\text{ortho/para}}}{h} = \frac{\frac{-2\mu_0 \mu_p^2 p^3}{(\sqrt{2}a_o)^3}}{h} \quad (11.365)$$

From Eq. (11.365) with  $p = 2$ , the ortho-para transition energy of the dihydrino molecule is 14.4 MHz.

## NUCLEAR MAGNETIC RESONANCE SHIFT

The proton gyromagnetic ratio,  $\gamma_p / 2\pi$ , is

$$\gamma_p / 2\pi = 42.57602 \text{ MHz } T^{-1} \quad (11.366)$$

The NMR frequency,  $f$ , is the product of the proton gyromagnetic ratio given by Eq. (11.366) and the magnetic flux,  $\mathbf{B}$ .

$$f = \gamma_p / 2\pi \mathbf{B} = 42.57602 \text{ MHz } T^{-1} \mathbf{B} \quad (11.367)$$

A typical flux for a superconducting NMR magnet is  $1.5 \text{ T}$ . According to Eq. (11.367) this corresponds to a radio frequency (RF) of  $63.86403 \text{ MHz}$ . With a constant magnetic field, the frequency is scanned to yield the spectrum where the frequency scan is typically achieved using a Fourier transform on the free induction decay signal following a radio frequency pulse. Or, in a less common type of NMR spectrometer, the radiofrequency is held constant (e.g.  $60 \text{ MHz}$ ), the applied magnetic field,  $H_0$  ( $H_0 = \frac{B}{\mu_0}$ ), is varied over a small range, and the frequency of energy absorption is recorded at the various values for  $H_0$ . The spectrum is typically scanned and displayed as a function of increasing  $H_0$ . The protons that absorb energy at a lower  $H_0$  give rise to a downfield absorption peak; whereas, the protons that absorb energy at a higher  $H_0$  give rise to an upfield absorption peak. The electrons of the compound of a sample influence the field at the nucleus such that it deviates slightly from the applied value. For the case that the chemical environment has no NMR effect, the value of  $H_0$  at resonance with the radiofrequency held constant at  $60 \text{ MHz}$  is

$$\frac{2\pi f}{\mu_0 \gamma_p} = \frac{(2\pi)(60 \text{ MHz})}{\mu_0 42.57602 \text{ MHz } T^{-1}} = H_0 \quad (11.368)$$

In the case that the chemical environment has a NMR effect, a different value of  $H_0$  is required for resonance. This chemical shift is proportional to the electronic magnetic flux charge at the nucleus due to the applied field, which in the case of each dihydrino molecule is a function of its semimajor and semiminor axes as shown *infra*.

Consider the application of a z-axis-directed uniform external magnetic flux,  $\mathbf{B}_z$ , to a dihydrino molecule comprising prolate spheroidal electron MOs with two spin-paired electrons. The diamagnetic reaction current increases or decreases the MO current to counteract any applied flux according to Lenz's law as shown in the Hydrino Hydride Ion Nuclear Magnetic Resonance Shift section. The current of hydrogen-type molecules is along

elliptical orbits parallel to the semimajor axis. Thus, the electronic interaction with the nuclei requires that each nuclear magnetic moment is in the direction of the semiminor axis. Thus, the nuclei are NMR active towards  $\mathbf{B}_z$  when the orientation of the semimajor axis,  $a$ , is along the x-axis, and the semiminor axes,  $b = c$ , are along the y-axis and z-axis, respectively.

- 5 The flux is applied over the time interval  $\Delta t = t_i - t_f$  such that the field increases at a rate  $dB/dt$ . The electric field,  $\mathbf{E}$ , along a perpendicular elliptic path of the dihydrino MO at the plane  $z = 0$  is given by

$$\oint \mathbf{E} \cdot d\mathbf{s} = \int \frac{dB}{dt} \cdot dA \quad (11.369)$$

- The induced electric field must be constant along the path; otherwise, compensating currents  
10 would flow until the electric field is constant. Thus, Eq. (11.369) becomes

$$E = \frac{\int \frac{dB}{dt} \cdot dA}{\oint ds} = \frac{\int \frac{dB}{dt} \cdot dA}{4aE(k)} = \frac{\pi ab \frac{dB}{dt}}{4aE(k)} \quad (11.370)$$

where  $E(k)$  is the elliptic integral given by

$$E(k) = \int_0^{\frac{\pi}{2}} \sqrt{1 - k^2 \sin^2 \phi} d\phi = 1.2375 \quad (11.371)$$

$$k = e = \frac{\sqrt{a^2 - b^2}}{a} = \frac{\sqrt{2}}{2} \quad (11.372)$$

- 15 the area of an ellipse,  $A$ , is

$$A = \pi ab \quad (11.373)$$

the perimeter of an ellipse,  $s$ , is

$$s = 4aE(k) \quad (11.374)$$

- $a$  is the semimajor axis given by Eq. (11.202),  $b$  is the semiminor axis given by Eq. (11.205), and  $e$  is the eccentricity given by Eq. (11.206). The acceleration along the path,  
20  $dv/dt$ , during the application of the flux is determined by the electric force on the charge density of the electrons:

$$m_e \frac{dv}{dt} = eE = \frac{e\pi ab}{4aE(k)} \frac{dB}{dt} \quad (11.375)$$

Thus, the relationship between the change in velocity,  $v$ , and the change in  $B$  is

$$25 \quad dv = \frac{e\pi ab}{4aE(k)m_e} dB \quad (11.376)$$

Let  $\Delta v$  represent the net change in  $v$  over the time interval  $\Delta t = t_i - t_f$  of the application of the flux. Then,

$$\Delta v = \int_{v_0}^{v_0 + \Delta v} dv = \frac{e\pi ab}{4aE(k)m_e} \int_0^B dB = \frac{e\pi abB}{4aE(k)m_e} \quad (11.377)$$

The average current,  $I$ , of a charge moving time harmonically along an ellipse is

$$5 \quad I = ef = \frac{ev}{4aE(k)} \quad (11.378)$$

where  $f$  is the frequency. The corresponding magnetic moment is given by

$$m = AI = \pi abI = \frac{\pi abev}{4aE(k)} \quad (11.379)$$

Thus, from Eqs. (11.377) and (11.379), the change in the magnetic moment,  $\Delta \mathbf{m}$ , due to an applied magnetic flux,  $\mathbf{B}$ , is [35]

$$10 \quad \Delta \mathbf{m} = -\frac{(e\pi ab)^2 \mathbf{B}}{(4aE(k))^2 m_e} \quad (11.380)$$

Next, the contribution from all plane cross sections of the prolate spheroid MO must be integrated along the z-axis. The spheroidal surface is given by

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{b^2} = 1 \quad (11.381)$$

The intersection of the plane  $z = z'$  ( $-b \leq z' \leq b$ ) with the spheroid determines the curve

$$15 \quad \frac{x^2}{a^2} + \frac{y^2}{b^2} = 1 - \frac{z'^2}{b^2} \quad (11.382)$$

or

$$\frac{x^2}{a^2 \left(1 - \frac{z'^2}{b^2}\right)} + \frac{y^2}{b^2 \left(1 - \frac{z'^2}{b^2}\right)} = 1 \quad (11.383)$$

Eq. (11.383) is an ellipse with semimajor axis,  $a'$ , and semiminor axis,  $b'$ , given by

$$a' = a \sqrt{1 - \frac{z'^2}{b^2}} \quad (11.384)$$

$$20 \quad b' = b \sqrt{1 - \frac{z'^2}{b^2}} \quad (11.385)$$

The eccentricity,  $e'$ , is given by

$$e' = \frac{\sqrt{a^2 \left(1 - \frac{z'^2}{b^2}\right) - b^2 \left(1 - \frac{z'^2}{b^2}\right)}}{a \sqrt{1 - \frac{z'^2}{b^2}}} = \frac{\sqrt{a^2 - b^2}}{a} = e \quad (11.386)$$

where  $e$  is given by Eq. (11.372). The area,  $A'$ , is given by

$$A' = \pi a' b' \quad (11.387)$$

and the perimeter,  $s'$ , is given by

$$s' = 4a' E(k) = 4aE(k) \sqrt{1 - \frac{z'^2}{b^2}} = s \sqrt{1 - \frac{z'^2}{b^2}} \quad (11.388)$$

where  $s$  is given by Eq. (11.374). The differential magnetic moment change along the  $z$ -axis is

$$d\Delta\mathbf{m} = -\frac{1}{2b} \frac{(e\pi a' b')^2 \mathbf{B}}{(4a' E(k))^2 m_e} dz' \quad (11.389)$$

Using Eq. (11.385) for the parameter  $b'$ , the change in magnetic moment for the dihydrino molecule is given by the integral over  $-b \leq b' \leq b$ :

$$\Delta\mathbf{m} = -\frac{1}{2b} \int_{-b}^b \frac{\left(e\pi a' b \sqrt{1 - \frac{z'^2}{b^2}}\right)^2 \mathbf{B}}{(4a' E(k))^2 m_e} dz' = -C_1 \frac{1}{m_e} \left(\frac{\pi e}{4E(k)}\right)^2 \quad (11.390)$$

Then, integral to correct for the  $z$ -dependence of  $b'$  is

$$C_1 = \frac{\int_{-b}^b (b^2 - z^2) dz}{2b} = \frac{2}{3} b^2 = \frac{a_0^2}{3p} \quad (11.391)$$

where the semiminor axis,  $b = \frac{a_0}{p\sqrt{2}}$ , given by Eq. (11.205) was used.

The change in magnetic moment would be given by the substitution of Eq. (11.391) into Eq. (11.390), if the change density were constant along the path of Eqs. (11.370) and (11.378), but it is not. The charge density of the MO in rectangular coordinates (Eq. (11.42)) is

$$\sigma = \frac{e}{4\pi abc} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \quad (11.392)$$

(The mass-density function of an MO is equivalent to its charge-density function where  $m$  replaces  $q$  of Eq. (11.42)). The equation of the plane tangent to the ellipsoid at the point  $x_0, y_0, z_0$  is

$$X \frac{x_0}{a^2} + Y \frac{y_0}{b^2} + Z \frac{z_0}{c^2} = 1 \quad (11.393)$$

5 where  $X, Y, Z$  are running coordinates in the plane. After dividing through by the square root of the sum of the squares of the coefficients of  $X, Y$ , and  $Z$ , the right member is the distance  $D$  from the origin to the tangent plane. That is,

$$D = \frac{1}{\sqrt{\frac{x_0^2}{a^4} + \frac{y_0^2}{b^4} + \frac{z_0^2}{c^4}}} \quad (11.394)$$

so that

$$10 \quad \sigma = \frac{e}{4\pi abc} D \quad (11.395)$$

In other words, the surface density at any point on the ellipsoidal MO is proportional to the perpendicular distance from the center of the ellipsoid to the plane tangent to the ellipsoid at the point. The charge is thus greater on the more sharply rounded ends farther away from the origin. In order to maintain current continuity, the diamagnetic velocity of Eq. (11.377) must  
15 be a constant along any given path integral corresponding to a constant electric field. Consequently, the charge density must be the minimum value of that given by Eq. (11.392). The minimum corresponds to  $y = b$  and  $x = z = 0$  such that the charge density is

$$\sigma = \frac{e}{4\pi ab^2} \frac{1}{\sqrt{\frac{0^2}{a^4} + \frac{b^2}{b^4} + \frac{0^2}{b^4}}} = \frac{e}{4\pi ab} \quad (11.396)$$

The MO is an equipotential surface, and the current must be continuous over the two-  
20 dimensional surface. Continuity of the surface current density,  $K$ , due to the diamagnetic effect of the applied magnetic field on the MO and the equipotential boundary condition require that the current of each elliptical curve determined by the intersection of the plane  $z = z'$  ( $-b \leq z' \leq b$ ) with the spheroid be the same. The charge density is spheroidally symmetrical about the semimajor axis. Thus,  $\lambda$ , the charge density per unit length along  
25 each elliptical path cross section of Eq. (11.383) is given by distributing the surface charge density of Eq. (11.396) uniformly along the  $z$ -axis for  $-b \leq z' \leq b$ . So,  $\lambda(z' = 0)$ , the linear charge density  $\lambda$  in the plane  $z' = 0$ , is



$$\lambda(z'=0) = \frac{\sigma}{\frac{1}{2b}} = \frac{e}{4\pi ab} 2b = \frac{e}{2\pi a} \quad (11.397)$$

And, the linear charge density must be equally distributed over each elliptical path cross section corresponding to each plane  $z = z'$ . The current is independent of  $z'$  when the linear charge density,  $\lambda(z')$ , is normalized for the path length:

$$5 \quad \lambda(z') = \frac{e}{2\pi a} \frac{4aE(k)}{4a'E(k')} = \frac{e}{2\pi a'} \quad (11.398)$$

where the equality of the eccentricities of each elliptical plane cross section given by Eq. (11.386) was used. Substitution of Eq. (11.388) for the corresponding charge density,

$\frac{e}{4a'E(k)}$ , of Eq. (11.390) and using Eq. (11.391) gives

$$\Delta \mathbf{m} = \frac{2}{3} \frac{e^2 b^2 \mathbf{B}}{4m_e} = \frac{e^2 a_0^2 \mathbf{B}}{12p^2 m_e} \quad (11.399)$$

10 The two electrons are spin-paired and the velocities are mirror opposites. Thus, the change in velocity of each electron treated individually (Eq. (10.3)) due to the applied field would be equal and opposite. However, as shown in the Three Electron Atom section, the two paired electrons may be treated as one with twice the mass where  $m_e$  is replaced by  $2m_e$  in Eq. (11.399). In this case, the paired electrons spin together about the applied field axis,  
15 the z-axis, to cause a reduction in the applied field according to Lenz's law. Thus, from Eq. (11.399), the change in magnetic moment is given by

$$\Delta \mathbf{m} = \frac{e^2 a_0^2 \mathbf{B}}{24p^2 m_e} \quad (11.400)$$

The opposing diamagnetic flux is uniform, parallel, and opposite the applied field as given by Stratton [36]. Specifically, the change in magnetic flux,  $\Delta \mathbf{B}$ , at the nucleus due to  
20 the change in magnetic moment,  $\Delta \mathbf{m}$ , is

$$\Delta \mathbf{B} = \mu_0 A_2 \Delta \mathbf{m} \quad (11.401)$$

where  $\mu_0$  is the permeability of vacuum,

$$A_2 = \int_0^\infty \frac{ds}{(s+b^2)R_s} \quad (11.402)$$

is an elliptic integral of the second kind given by Whittaker and Watson [37], and

$$25 \quad R_s = (s+b^2)\sqrt{(s+a^2)} \quad (11.403)$$

Substitution of Eq. (11.403) into Eq. (11.402) gives

$$A_2 = \int_0^{\infty} \frac{ds}{(s+b^2)^2 (s+a^2)^{1/2}} \quad (11.404)$$

From integral 154 of Lide [38]:

$$A_2 = - \left\{ \frac{1}{a^2-b^2} \frac{\sqrt{s+a^2}}{s+b^2} \right\}_0^{\infty} - \frac{1}{2} \frac{1}{a^2-b^2} \int_0^{\infty} \frac{ds}{(s+b^2)\sqrt{s+a^2}} \quad (11.405)$$

5 The evaluation at the limits of the first integral is

$$- \left\{ \frac{1}{a^2-b^2} \frac{\sqrt{s+a^2}}{s+b^2} \right\}_0^{\infty} = \frac{a}{b^2(a^2-b^2)} \quad (11.406)$$

From integral #147 of Lide [9], the second integral is:

$$- \frac{1}{2} \frac{1}{a^2-b^2} \int_0^{\infty} \frac{ds}{(s+b^2)\sqrt{s+a^2}} = \left\{ \frac{1}{2(a^2-b^2)^{3/2}} \ln \frac{\sqrt{s+a^2} + \sqrt{a^2-b^2}}{\sqrt{s+a^2} - \sqrt{a^2-b^2}} \right\}_0^{\infty} \quad (11.407)$$

Evaluation at the limits of the second integral gives

$$10 \quad - \frac{1}{2} \frac{1}{(a^2-b^2)^{3/2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \quad (11.408)$$

Combining Eq. (11.406) and Eq. (11.408) gives

$$A_2 = \frac{a}{b^2(a^2-b^2)} - \frac{1}{2} \frac{1}{(a^2-b^2)^{3/2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \frac{p^3 4}{a_0^3} - \frac{p^3 \sqrt{2}}{a_0^3} \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} \quad (11.409)$$

where the semimajor axis,  $a = \frac{a_0}{p}$ , given by Eq. (11.202) and the semiminor axis,  $b = \frac{a_0}{p\sqrt{2}}$ ,

given by Eq. (11.205) were used.

15 Substitution of Eq. (11.400) and Eq. (11.409) into Eq. (11.401) gives

$$\Delta \mathbf{B} = -\mu_0 \left( \frac{p^3 4}{a_0^3} - \frac{p^3 \sqrt{2}}{a_0^3} \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} \right) \frac{a_0^2 e^2 \mathbf{B}}{24 p^2 m_e} \quad (11.410)$$

Additionally, it is found both theoretically and experimentally that the dimensions,  $r^2$ , of the molecule corresponding to the area in Eqs. (11.369) and (11.379) used to derived Eq. (11.410) must be replaced by an average,  $\langle r^2 \rangle$ , that takes into account averaging over the

20 orbits isotropically oriented. The correction of 2/3 is given by Purcell [35]. In the case of hydrogen-type molecules, the electronic interaction with the nuclei require that each nuclear magnetic moment is in the direction of the semiminor axis. But free rotation about each of

three axes results in an isotropic averaging of 2/3 where the rotational frequencies of hydrogen-type molecules are much greater than the corresponding NMR frequency (e.g.  $10^{12}$  Hz versus  $10^8$  Hz). Thus, Eq. (11.410) gives the absolute upfield chemical shift,  $\frac{\Delta B}{B}$ , of  $H_2$  relative to a bare proton:

$$\begin{aligned}
 \frac{\Delta B}{B} &= \frac{\Delta B}{B} = -\mu_0 \left( \frac{p^3 4}{a_0^3} - \frac{p^3 \sqrt{2}}{a_0^3} \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} \right) \frac{a_0^2 e^2}{36 p^2 m_e} \\
 &= -\mu_0 \left( 4 - \sqrt{2} \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} \right) \frac{p e^2}{36 a_0 m_e} \\
 &= -p 28.01 \text{ ppm}
 \end{aligned} \tag{11.411}$$

where  $p=1$  for  $H_2$ .

It follows from Eqs. (11.202) and (11.411) that the diamagnetic flux (flux opposite to the applied field) at each nucleus is inversely proportional to the semimajor radius,  $a = \frac{a_0}{p}$ .

For resonance to occur,  $\Delta H_0$ , the change in applied field from that given by Eq. (11.368), must compensate by an equal and opposite amount as the field due to the electrons of the dihydrino molecule. According to Eq. (11.202), the ratio of the semimajor axis of the dihydrino molecule  $H_2(1/p)$  to that of the hydrogen molecule  $H_2$  is the reciprocal of an integer  $p$ . Similarly it is shown in the Hydrino Hydride Ion Nuclear Magnetic Resonance Shift section and previously [39], that according to Eq. (7.87) the ratio of the radius of the hydrino hydride ion  $H^-(1/p)$  to that of the hydride ion  $H^-(1/1)$  is the reciprocal of an integer  $p$ . It follows from Eqs. (7.90-7.96) that compared to a proton with no chemical shift, the ratio of  $\Delta H_0$  for resonance of the proton of the hydrino hydride ion  $H^-(1/p)$  to that of the hydride ion  $H^-(1/1)$  is a positive integer. That is, if only the radius is considered, the absorption peak of the hydrino hydride ion occurs at a value of  $\Delta H_0$  that is a multiple of  $p$  times the value that is resonant for the hydride ion compared to that of a proton with no shift. However, a hydrino hydride ion is equivalent to the ordinary hydride ion except that it is in a lower energy state. The source current of the state must be considered in addition to the reduced radius.

As shown in the Stability of "Ground" and Hydrino States section, for the below "ground" (fractional quantum number) energy states of the hydrogen atom,  $\sigma_{\text{photon}}$ , the two-

dimensional surface charge due to the "trapped photon" at the electron orbitsphere and phase-locked with the electron orbitsphere current, is given by Eqs. (5.08) and (2.11).

$$\sigma_{\text{photon}} = \frac{e}{4\pi(r_n)^2} \left[ Y_0^0(\theta, \phi) - \frac{1}{n} \left[ Y_0^0(\theta, \phi) + \text{Re} \{ Y_\ell^m(\theta, \phi) e^{i\omega_n t} \} \right] \right] \delta(r - r_n)$$

$$n = \frac{1}{p} = 1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \dots, \quad (11.412)$$

5 And,  $\sigma_{\text{electron}}$ , the two-dimensional surface charge of the electron orbitsphere is

$$\sigma_{\text{electron}} = \frac{-e}{4\pi(r_n)^2} \left[ Y_0^0(\theta, \phi) + \text{Re} \{ Y_\ell^m(\theta, \phi) e^{i\omega_n t} \} \right] \delta(r - r_n) \quad (11.413)$$

The superposition of  $\sigma_{\text{photon}}$  (Eq. (11.412)) and  $\sigma_{\text{electron}}$ , (Eq. (11.413)) where the spherical harmonic functions satisfy the conditions given in the Angular Function section is

$$\sigma_{\text{photon}} + \sigma_{\text{electron}} = \frac{-e}{4\pi(r_n)^2} \left[ \frac{1}{n} Y_0^0(\theta, \phi) + \left( 1 + \frac{1}{n} \right) \text{Re} \{ Y_\ell^m(\theta, \phi) e^{i\omega_n t} \} \right] \delta(r - r_n)$$

$$n = \frac{1}{p} = 1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \dots, \quad (11.414)$$

10

The ratio of the total charge distributed over the surface at the radius of the hydrino hydride ion  $H^-(1/p)$  to that of the hydride ion  $H^-(1/1)$  is an integer  $p$ , and the corresponding total source current of the hydrino hydride ion is equivalent to an integer  $p$  times that of an electron. The "trapped photon" obeys the phase-matching condition given in Excited States  
 15 of the One-Electron Atom (Quantization) section, but does not interact with the applied flux directly. Only each electron does; thus,  $\Delta v$  of Eq. (11.377) must be corrected by a factor of  $1/p$  corresponding to the normalization of the electron source current according to the invariance of charge under Gauss' Integral Law. As also shown by Eqs. (7.17-7.23) and (7.87), the "trapped photon" gives rise to a correction to the change in magnetic moment due  
 20 to the interaction of each electron with the applied flux. The correction factor of  $1/p$  consequently cancels the NMR effect of the reduced radius which is consistent with general observations on diamagnetism [40]. It follows that the same result applies in the case of Eq. (11.411) for  $H_2(1/p)$  wherein the coordinates are ellipsoidal rather than spherical.

The cancellation of the chemical shift due to the reduced radius or the reduced  
 25 semiminor and semimajor axes in the case of  $H^-(1/p)$  and  $H_2(1/p)$ , respectively, by the corresponding source current is exact except for an additional relativistic effect. The relativistic effect for  $H^-(1/p)$  arises due to the interaction of the currents corresponding to

the angular momenta of the "trapped photon" and the electrons and is analogous to that of the fine structure of the hydrogen atom involving the  $^2P_{3/2} \rightarrow ^2P_{1/2}$  transition. The derivation follows that of the fine structure given in the Spin-Orbital Coupling section.

$\frac{e}{m_e}$  of the electron, the electron angular momentum of  $\hbar$ , and the electron magnetic

5 momentum of  $\mu_B$  are invariant for any electronic state. The same applies for the paired electrons of hydrino hydride ions. The condition that flux must be linked by the electron in units of the magnetic flux quantum in order to conserve the invariant electron angular momentum of  $\hbar$  gives the additional chemical shift due to relativistic effects. Using Eqs. (2.159-2.160), Eq. (2.166) may be written as

$$10 \quad E_{s/o} = \frac{\alpha \pi \mu_0 e^2 \hbar^2}{m_e^2 r^3} \sqrt{\frac{3}{4}} = \alpha 2\pi 2 \frac{e\hbar}{2m_e} \frac{\mu_0 e\hbar}{2m_e a_0^3} \sqrt{\frac{3}{4}} = \alpha 2\pi 2 \mu_B B \quad (11.415)$$

From Eq. (11.415) and Eq. (1.205), the relativistic stored magnetic energy contributes a factor of  $\alpha 2\pi$ . In spherical coordinates, the relativistic change in flux  $\Delta \mathbf{B}_{SR}$  may be calculated using Eq. (7.95) and the relativistic factor of  $\gamma_{SR} = 2\pi\alpha$  which is the same as that given by Eq. (1.229):

$$15 \quad \Delta \mathbf{B}_{SR} = -\gamma_{SR} \mu_0 \frac{\Delta m}{r_n^3} (\mathbf{i}_r \cos \theta - \mathbf{i}_\theta \sin \theta) = -2\pi\alpha \mu_0 \frac{\Delta m}{r_n^3} (\mathbf{i}_r \cos \theta - \mathbf{i}_\theta \sin \theta) \quad (11.416)$$

for  $r < r_n$ .

The stored magnetic energy term of the electron  $g$  factor of each electron of a dihydrino molecule is the same as that of a hydrogen atom since  $\frac{e}{m_e}$  is invariant and the

invariant angular momentum and magnetic moment of the former are also  $\hbar$  and  $\mu_B$ ,

20 respectively, as given in the Magnetic Moment of an Ellipsoidal MO and Magnetic Field of an Ellipsoidal MO sections. Thus, the corresponding correction in ellipsoidal coordinates follows from Eq. (2.166) wherein the result of the length contraction for the circular path in spherical coordinates is replaced by that of the elliptical path.

The only position on the elliptical path at which the current is perpendicular to the  
25 radial vector defined by the central force of the protons is at the semimajor axis. It was shown in the Special Relativistic Correction to the Ionization Energies section that when the condition that the electron's motion is tangential to the radius is met, the radius is Lorentzian invariant. That is, for the case that  $k$  is the lightlike  $k^0$ , with  $k = \omega_n / c$ ,  $a$  is invariant. In

the case of a spherically symmetrical MO such as the case of the hydrogen atom, it was also shown that this condition determines that the electron's angular momentum of  $\hbar$ ,  $\frac{e}{m_e}$  of Eq.

(1.110), and the electron's magnetic moment of a Bohr magneton,  $\mu_B$ , are invariant. The effect of the relativistic length contraction and time dilation for constant spherical motion is a change in the angle of motion with a corresponding decrease in the electron wavelength. The angular motion becomes projected onto the radial axis which contracts, and the extent of the decrease in the electron wavelength and radius due to the electron motion in the laboratory inertial frame are given by

$$\lambda = 2\pi r' \sqrt{1 - \left(\frac{v}{c}\right)^2} \sin \left[ \frac{\pi}{2} \left( 1 - \left(\frac{v}{c}\right)^2 \right)^{3/2} \right] + r' \cos \left[ \frac{\pi}{2} \left( 1 - \left(\frac{v}{c}\right)^2 \right)^{3/2} \right] \quad (11.417)$$

10 and

$$r = r' \left[ \sqrt{1 - \left(\frac{v}{c}\right)^2} \sin \left[ \frac{\pi}{2} \left( 1 - \left(\frac{v}{c}\right)^2 \right)^{3/2} \right] + \frac{1}{2\pi} \cos \left[ \frac{\pi}{2} \left( 1 - \left(\frac{v}{c}\right)^2 \right)^{3/2} \right] \right] \quad (11.418)$$

respectively. Then, the relativistic factor  $\gamma^*$  is

$$\gamma^* = \frac{2\pi}{2\pi \sqrt{1 - \left(\frac{v}{c}\right)^2} \sin \left[ \frac{\pi}{2} \left( 1 - \left(\frac{v}{c}\right)^2 \right)^{3/2} \right] + \cos \left[ \frac{\pi}{2} \left( 1 - \left(\frac{v}{c}\right)^2 \right)^{3/2} \right]} \quad (11.419)$$

where the velocity is given by Eq. (1.56) with the radius given by Eq. (1.233).

15 Each point or coordinate position on the continuous two-dimensional electron MO of the dihydrino molecule defines an infinitesimal mass-density element which moves along an elliptical orbit of a spheroidal MO in such a way that its eccentric angle,  $\theta$ , changes at a constant rate. That is  $\theta = \omega t$  at time  $t$  where  $\omega$  is a constant, and

$$r(t) = \mathbf{i}a \cos \omega t + \mathbf{j}b \sin \omega t \quad (11.420)$$

20 is the parametric equation of the ellipse. Next, special relativistic effects on distance and time are considered. The parametric radius,  $r(t)$ , is a minimum at the position of the semiminor axis of length  $b$ , and the motion is transverse to the radial vector. Since the angular momentum of  $\hbar$  is constant, the electron wavelength without relativistic correction is given by

$$25 \quad 2\pi b = \lambda = \frac{h}{mv} \quad (11.421)$$

such that the angular momentum,  $L$ , is given by

$$L = r \times mv = bmv = \hbar \quad (11.422)$$

The nonradiation and the  $\hbar$ ,  $\frac{e}{m_e}$ , and  $\mu_B$  invariance conditions require that the angular frequencies,  $\omega_s$  and  $\omega_e$ , for spherical and ellipsoidal motion, respectively, are

$$\omega_s = \frac{\hbar}{m_e r^2} = \frac{\frac{\pi L}{m_e}}{A} \quad (11.423)$$

5 and

$$\omega_e = \frac{\pi \hbar}{m_e A} = \frac{\hbar}{m_e ab} \quad (11.424)$$

where  $A$  is the area of the closed orbit, the area of an ellipse given by Eq. (11.373). Since the angular frequency  $\omega_e$  has the form as  $\omega_s$ , the time dilation corrections are equivalent, where the correction for  $\omega_s$  is given in the Special Relativistic Correction to the Ionization Energies  
 10 section. Since the semimajor axis,  $a$ , is invariant, but  $b$  undergoes length contraction, the relationship between the velocity and the electron wavelength at the semiminor axis from Eq. (11.417) and Eq. (11.421) is

$$\lambda = 2\pi b \sqrt{1 - \left(\frac{v}{c}\right)^2} \sin \left[ \frac{\pi}{2} \left( 1 - \left(\frac{v}{c}\right)^2 \right)^{3/2} \right] + a \cos \left[ \frac{\pi}{2} \left( 1 - \left(\frac{v}{c}\right)^2 \right)^{3/2} \right] \quad (11.425)$$

where  $\lambda \rightarrow a$  as  $v \rightarrow c$  replaces the spherical coordinate result of  $\lambda \rightarrow r'$  as  $v \rightarrow c$ . Thus, in  
 15 the electron frame at rest  $v = 0$ , and, Eq. (11.425) becomes

$$\lambda' = 2\pi b \quad (11.426)$$

In the laboratory inertial frame for the case that  $v = c$  in Eq. (11.425),  $\lambda$  is

$$\lambda = a \quad (11.427)$$

Thus, using Eqs. (11.426) and (11.427), the relativistic factor,  $\gamma^*$ , is

$$20 \quad \gamma^* = \frac{\lambda}{\lambda'} = \frac{a}{2\pi b} \quad (11.428)$$

From Eqs. (11.417-11.419) and Eq. (11.428), the relativistic diamagnetic effect of the inverse integer radius of  $H_2(1/p)$  compared to  $H_2$ , each with ellipsoidal MOs, is equivalent to the ratio of the semiminor and semimajor axes times the correction for the spherical orbital case given in Eq. (11.416). From the mass (Eq. (2.165)) and radius corrections (Eq. (2.163))  
 25 in Eq. (2.166), the relativistic stored magnetic energy contributes a factor  $\gamma_{SR}$  of

$$\gamma_{SR} = 2\pi\alpha \left(\frac{b}{a}\right)^2 = \pi\alpha \quad (11.429)$$

Thus, from Eqs. (11.401), (11.416), and (11.429), the relativistic change in flux,  $\Delta\mathbf{B}_{SR}$ , for the dihydrino molecule  $H_2(1/p)$  is

$$\Delta\mathbf{B}_{SR} = -\gamma_{SR}\mu_0 A_2 \Delta\mathbf{m} = -\pi\alpha\mu_0 A_2 \Delta\mathbf{m} \quad (11.430)$$

5 Thus, using Eq. (11.411) and Eq. (11.430), the upfield chemical shift,  $\frac{\Delta B_{SR}}{B}$ , due to the relativistic effect of the molecule  $H_2(1/p)$  corresponding to the lower-energy state with principal quantum energy state  $p$  is given by

$$\frac{\Delta B_{SR}}{B} = -\mu_0\pi\alpha \left(4 - \sqrt{2} \ln \frac{\sqrt{2}+1}{\sqrt{2}-1}\right) \frac{pe^2}{36a_0m_e} \quad (11.431)$$

The total shift,  $\frac{\Delta B_T}{B}$ , for  $H_2(1/p)$  is given by the sum of that of  $H_2$  given by Eq. (11.411)

10 with  $p=1$  plus that given by Eq. (11.431):

$$\frac{\Delta B_T}{B} = -\mu_0 \left(4 - \sqrt{2} \ln \frac{\sqrt{2}+1}{\sqrt{2}-1}\right) \frac{e^2}{36a_0m_e} (1 + \pi\alpha p) \quad (11.432)$$

$$\frac{\Delta B_T}{B} = -(28.01 + 0.64p) \text{ ppm} \quad (11.433)$$

where  $p = \text{integer} > 1$ .

$H_2$  has been characterized by gas phase  $^1H$  NMR. The experimental absolute  
15 resonance shift of gas-phase TMS relative to the proton's gyromagnetic frequency is -28.5 ppm [30].  $H_2$  was observed at 0.48 ppm compared to gas phase TMS set at 0.00 ppm [31]. Thus, the corresponding absolute  $H_2$  gas-phase resonance shift of -28.0 ppm (-28.5 + 0.48) ppm was in excellent agreement with the predicted absolute gas-phase shift of -28.01 ppm given by Eq. (11.411).

20

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## Section II

### GENERAL DIATOMIC AND POLYATOMIC MOLECULAR IONS AND MOLECULES

5 Non-hydrogen diatomic and polyatomic molecular ions and molecules can be solved using the same principles as those used to solve hydrogen molecular ions and molecules wherein the hydrogen molecular orbitals (MOs) and hydrogen atomic orbitals serve as basis functions for the MOs of the general diatomic and polyatomic molecular ions or molecules. The MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) 10 correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron angular momentum of  $\hbar$ . Energy of the MO must be matched to that of the outermost atomic orbital of a bonding heteroatom in the case where a minimum energy is achieved with a direct bond to the atomic orbital (AO). In the case that an independent 15 MO is formed, the AO force balance causes the remaining electrons to be at lower energy and a smaller radius. The atomic orbital may hybridize in order to achieve a bond at an energy minimum. At least one molecule or molecular ion representative of each of these cases was solved. Specifically, the results of the determination of bond parameters of  $H_3^+$ ,  $D_3^+$ ,  $OH$ ,  $OD$ ,  $H_2O$ ,  $D_2O$ ,  $NH$ ,  $ND$ ,  $NH_2$ ,  $ND_2$ ,  $NH_3$ ,  $ND_3$ ,  $CH$ ,  $CD$ ,  $CH_2$ ,  $CH_3$ ,  $CH_4$ ,  $N_2$ , 20  $O_2$ ,  $F_2$ ,  $Cl_2$ ,  $CN$ ,  $CO$ , and  $NO$  are given in Table 13.1. The calculated results for homo- and hetero-diatomic radicals and molecules, and polyatomic molecular ions and molecules are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

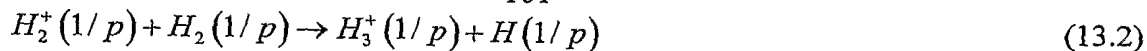
25

#### TRIATOMIC MOLECULAR HYDROGEN-TYPE ION ( $H_3^+$ )

The polyatomic molecular ion  $H_3^+(1/p)$  is formed by the reaction of a proton with a hydrogen-type molecule



30 and by the exothermic reaction



### FORCE BALANCE OF $H_3^+$ -TYPE MOLECULAR IONS

$H_3^+(1/p)$ -type molecular ions comprise two indistinguishable spin-paired electrons bound by three protons. The ellipsoidal molecular orbital (MO) satisfies the boundary constraints as shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. Since the protons are indistinguishable, ellipsoidal MOs about each pair of protons taken one at a time are indistinguishable.  $H_3^+(1/p)$  is then given by a superposition or linear combinations of three equivalent ellipsoidal MOs that form an equilateral triangle where the points of contact between the prolate spheroids are equivalent in energy and charge density. The outer perimeter of the superposition of three prolate spheroids is the  $H_3^+(1/p)$  MO with the protons at the foci that bind and maintain the electron MO.

As in the case for  $H_2^+(1/p)$  and  $H_2(1/p)$  shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section, the stability of  $H_3^+(1/p)$  is due to the dependence of the charge density of the distance  $D$  from the origin to the tangent plane. That is,

$$D = \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \quad (13.3)$$

so that

$$\sigma = \frac{e}{4\pi ab^2} D \quad (13.4)$$

In other words, the surface density at any point on a charged ellipsoidal conductor is proportional to the perpendicular distance from the center of the ellipsoid to the plane tangent to the ellipsoid at the point. The charge is thus greater on the more sharply rounded ends farther away from the origin. This distribution places the charge closest to the protons to give a minimum energy.

The balanced forces also depend on  $D$  as shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. The  $D$ -dependence of the charge density as well as the centrifugal and Coulombic central field of two nuclei at the foci of the ellipsoid applies to each ellipsoid which is given from any other by a rotation of  $|\phi| = \frac{\pi}{3}$  about an axis at a focus

that is perpendicular to the plane of the equilateral triangle defined by the three foci. Since the centrifugal, Coulombic, and magnetic forces relate mass and charge densities which are interchangeable by the ratio  $e/m_e$ , the conditions at any point on any given ellipsoid is applicable to any other point on the ellipsoid. Furthermore, this condition can be generalized to any point of the other members of the set of three ellipsoids due to equivalence. As a further constraint to maintain the force balance between the three protons and the  $H_3^+(1/p)$  MO comprising the superposition of the three  $H_2(1/p)$ -type ellipsoidal MOs, the total charge of the two electrons must be normalized over the three basis set  $H_2(1/p)$ -type ellipsoidal MOs. In this case, the parameters of each basis element  $H_2(1/p)$ -type ellipsoidal MO is solved, and the energies are given by the electron charge where it appears multiplied by a factor of 3/2 (three MOs normalized by the total charge of two electrons).

Consider each  $H_2(1/p)$ -type ellipsoidal MO. At each point on the  $H_3^+(1/p)$  MO, the electron experiences a centrifugal force, and the balancing centripetal force (on each electron) is produced by the electric force between the electron and the ellipsoidal electric field and the radiation-reaction-type magnetic force between the two electrons causing the electrons to pair. The force balance equation derived in Force Balance of Hydrogen-Type Molecules section is given by Eq. (11.200):

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{p e^2}{8\pi \epsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.5)$$

$$\frac{2a_0}{pa} - \frac{a_0}{pa} = 1 \quad (13.6)$$

$$a = \frac{a_0}{p} \quad (13.7)$$

Substitution of Eq. (13.7) into Eq. (11.79) is

$$c' = \frac{1}{p\sqrt{2}} a_0 \quad (13.8)$$

The internuclear distance given by multiplying Eq. (13.8) by two is

$$2c' = \frac{a_0 \sqrt{2}}{p} \quad (13.9)$$

Substitution of Eqs. (13.7-13.8) into Eq. (11.80) is

$$b = c = \frac{1}{p\sqrt{2}} a_0 \quad (13.10)$$

Substitution of Eqs. (13.7-13.8) into Eq. (11.67) is

$$e = \frac{1}{\sqrt{2}} \quad (13.11)$$

Using the parameters given by Eqs. (13.7-13.11), the resulting  $H_3^+(1/p)$  MO comprising the superposition of three  $H_2(1/p)$ -type ellipsoidal MOs is shown in Figure 6. The outer surface of the superposition comprises charge density of the MO. The equilateral triangular structure was confirmed experimentally [1]. The  $H_3^+(1/p)$  MO having no distinguishable electrons is consistent with the absence of strong excited states observed for  $H_3^+$  [1]. It is also consistent with the absence of a permanent dipole moment [1].

## 10 ENERGIES OF $H_3^+$ -TYPE MOLECULAR IONS

The due to the equivalence of the  $H_2(1/p)$ -type ellipsoidal MOs and the linear superposition of their energies, the energy components defined previously for the molecule, Eqs. (11.207-11.212) apply in the case of the corresponding  $H_3^+(1/p)$  molecular ion. And, each molecular energy component is given by the integral of corresponding force in Eq. (13.5). Each energy component is the total for the two equivalent electrons with the exception that the total charge of the two electrons is normalized over the three basis set  $H_2(1/p)$ -type ellipsoidal MOs. Thus, the energies are those given for  $H_2(1/p)$  in the Energies of Hydrogen-Type Molecules section with the electron charge, where it appears, multiplied by a factor of  $3/2$ . In addition, the three sets of equivalent proton-proton pairs give rise to a factor of three times the proton-proton repulsion energy given by Eq. (11.208). The parameters  $a$  and  $b$  are given by Eqs. (13.7) and (13.10), respectively.

$$V_e = \frac{3}{2} \frac{-2pe^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \quad (13.12)$$

$$V_p = 3 \frac{p}{8\pi\epsilon_0} \frac{e^2}{\sqrt{a^2-b^2}} \quad (13.13)$$

$$T = \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \quad (13.14)$$

The energy,  $V_m$ , corresponding to the magnetic force of Eq. (13.5) is

$$V_m = \frac{3}{2} \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \quad (13.15)$$

$$E_T = V_e + T + V_m + V_p \quad (13.16)$$

$$E_T = -\frac{e^2}{8\pi\epsilon_0 a_0} \left[ \left( 3p^2\sqrt{2} - p^2\sqrt{2} + 3\frac{p^2\sqrt{2}}{4} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - 3p^2\sqrt{2} \right] = -p^2 35.54975 \text{ eV} \quad (13.17)$$

5 where the charge  $e$  appears in the magnetic energy  $V_m$  according to Eqs. (7.14-7.24) as discussed in the Force Balance of Hydrogen-Type Molecules section.

### VIBRATION OF $H_3^+$ -TYPE MOLECULAR IONS

The vibrational energy levels of  $H_3^+$ -type molecular ions may be solved as three equivalent  
 10 coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

### 15 THE DOPPLER ENERGY TERM OF $H_3^+$ -TYPE MOLECULAR IONS

As shown in the Vibration of Hydrogen-type Molecular Ions section, the electron orbiting the nuclei at the foci of an ellipse may be perturbed such that a stable reentrant orbit is established that gives rise to a vibrational state corresponding to time harmonic oscillation of the nuclei and electron. The perturbation is caused by a photon that is resonant with the  
 20 frequency of oscillation of the nuclei wherein the radiation is electric dipole with the corresponding selection rules.

Oscillation may also occur in the transition state. The perturbation arises from the decrease in internuclear distance as the molecular bond forms. Relative to the unperturbed case given in the Force Balance of Hydrogen-type Molecular Ions section, the reentrant orbit  
 25 may give rise to a decrease in the total energy while providing a transient kinetic energy to the vibrating nuclei. However, as an additional condition for stability, radiation must be considered. A nonradiative state must be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied. The radiation reaction force due to the vibration of  $H_2^+(1/p)$  and  $H_2(1/p)$  in the transition state



was derived in the Doppler Energy Term of Hydrogen-type Molecular Ions section and the Doppler Energy Term of Hydrogen-type Molecules section, respectively, and corresponds to a Doppler energy,  $E_D$ , that is dependent on the motion of the electron and the nuclei. The radiation reaction force in the case of the vibration of  $H_3^+(1/p)$  in the transition state also corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. Here, a nonradiative state must also be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied. Typically, a third body is required to form  $H_3^+$ -type molecular ions. For example, the exothermic chemical reaction of  $H + H$  to form  $H_2$  does not occur with the emission of a photon. Rather, the reaction requires a collision with a third body,  $M$ , to remove the bond energy-  $H + H + M \rightarrow H_2 + M^*$  [3]. The third body distributes the energy from the exothermic reaction, and the end result is the  $H_2$  molecule and an increase in the temperature of the system. Thus, a third body removes the energy corresponding to the additional force term given by Eq. (11.180).

The kinetic energy of the transient vibration is derived from the corresponding central forces. From Eqs. (13.5) and (13.12), the central force terms between the electron MO and the protons of each of the three  $H_2(1/p)$ -type ellipsoidal MOs are

$$f(a) = -\frac{3}{2} \frac{pe^2}{4\pi\epsilon_0 a^2} \quad (13.18)$$

and

$$f'(a) = \frac{3}{2} \frac{2pe^2}{4\pi\epsilon_0 a^3} \quad (13.19)$$

Thus, using Eqs. (11.136) and (13.18-13.19), the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\frac{3}{2} \frac{pe^2}{4\pi\epsilon_0 \left(\frac{a_0}{p}\right)^3}}{m_e}} = p^2 5.06326 \times 10^{16} \text{ rad/s} \quad (13.20)$$

where the semimajor axis,  $a$ , is  $a = \frac{a_0}{p}$  according to Eq. (13.7). The kinetic energy,  $E_K$ , is

given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar p^2 5.06326 \times 10^{16} \text{ rad/s} = p^2 33.3273 \text{ eV} \quad (13.21)$$

In Eq. (11.181), substitution of the total energy of the  $H_3^+$ -type molecular ion,  $E_T$ , (Eq. (13.17)) for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.21) for  $\bar{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit.

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -35.54975 p^2 \text{ eV} \sqrt{\frac{2e(p^2 33.3273 \text{ eV})}{m_e c^2}} = -p^3 0.406013 \text{ eV} \quad (13.22)$$

5 The total energy of the  $H_3^+$ -type molecular ion is decreased by  $\bar{E}_D$ .

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [4]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons,  $\bar{E}_{Kvib}$ , is 1/2

10 of the vibrational energy of the  $H_3^+$ -type molecular ion given by Eq. (11.148). The decrease in the energy of the molecular ion due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  and  $\bar{E}_{Kvib}$ . Using Eq. (13.22) and the experimental vibrational energy  $H_3^+$  of  $E_{vib} = 2521.31 \text{ cm}^{-1} = 0.312605 \text{ eV}$  [1] gives

$$15 \quad \bar{E}_{osc} = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar p^2 \sqrt{\frac{k}{\mu}} \quad (13.23)$$

$$\bar{E}_{osc} = -p^3 0.406013 \text{ eV} + \frac{1}{2} p^2 (0.312605 \text{ eV}) \quad (13.24)$$

The reentrant orbit for the binding of a proton to  $H_2(1/p)$  causes two bonds to oscillate by increasing and decreasing in length along opposite sides of the equilateral triangle at a relative phase angle of  $180^\circ$ . Since the vibration and reentrant oscillation is along two

20 lengths of the equilateral triangular MO with  $E$  symmetry,  $\bar{E}_{osc}$  for  $H_3^+(1/p)$ ,  $\bar{E}_{osc}(H_3^+(1/p))$ , is:

$$\begin{aligned} \bar{E}_{osc}(H_3^+(1/p)) &= 2 \left( \bar{E}_D + \frac{1}{2} \hbar p^2 \sqrt{\frac{k}{\mu}} \right) \\ &= 2 \left( -p^3 0.406013 \text{ eV} + \frac{1}{2} p^2 (0.312605 \text{ eV}) \right) \end{aligned} \quad (13.25)$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies,  $\bar{E}_K$ , are the same independent of the isotope of hydrogen, but the vibrational

energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies per bond. Using Eq. (13.22), Eq. (13.25), and the experimental vibrational energy  $D_3^+$  of  $E_{vib} = 1834.67 \text{ cm}^{-1} = 0.227472 \text{ eV}$  [1], the corresponding  $\bar{E}_{osc}(D_3^+(1/p))$  is

$$5 \quad \bar{E}_{osc}(D_3^+(1/p)) = 2 \left( -p^3 0.406013 \text{ eV} + \frac{1}{2} p^2 (0.227472 \text{ eV}) \right) \quad (13.26)$$

### TOTAL AND BOND ENERGIES OF $H_3^+(1/p)$ - AND $D_3^+(1/p)$ -TYPE MOLECULAR IONS

The total energy of the  $H_3^+(1/p)$ -type molecular ion is given by the sum of  $E_T$  (Eqs. (13.16-10 13.17)) and  $\bar{E}_{osc}(H_3^+(1/p))$  given Eqs. (13.20-13.25). Thus, the total energy of  $H_3^+(1/p)$  having a central field of  $+pe$  at each focus of the prolate spheroid molecular orbital including the Doppler term is

$$E_T = V_e + T + V_m + V_p + \bar{E}_{osc}(H_3^+(1/p)) \quad (13.27)$$

$$15 \quad E_T = -p^2 \left\{ \frac{e^2}{8\pi\epsilon_0 a_0} \left[ \left( 3\sqrt{2} - \sqrt{2} + \frac{3\sqrt{2}}{4} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - 3\sqrt{2} \right] \left[ 1 + 2p \sqrt{\frac{2\hbar \sqrt{\frac{3}{2} \frac{e^2}{4\pi\epsilon_0 a_0^3}}}{m_e c^2}} \right] - 2 \left( \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \right\} \\ = -p^2 35.54975 - 2p^3 0.406013 \text{ eV} + 2p^2 \left( \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \quad (13.28)$$

From Eqs. (13.24-13.25) and (13.27-13.28), the total energy of the  $H_3^+$ -type molecular ion is

$$\begin{aligned} E_T &= -p^2 35.54975 \text{ eV} + \bar{E}_{osc}(H_3^+(1/p)) \\ &= -p^2 35.54975 - 2p^3 0.406013 \text{ eV} + 2 \left( \frac{1}{2} p^2 (0.312605 \text{ eV}) \right) \\ &= -p^2 35.23714 \text{ eV} - p^3 0.812025 \text{ eV} \end{aligned} \quad (13.29)$$

The total energy of the  $D_3^+$ -type molecular ion is given by the sum of  $E_T$  (Eq. (13.17)) and 20  $\bar{E}_{osc}(D_3^+(1/p))$  given by Eq. (13.26):

$$\begin{aligned}
E_T &= -p^2 35.54975 \text{ eV} + \bar{E}_{osc} \left( D_3^+ (1/p) \right) \\
&= -p^2 35.54975 - 2p^3 0.406013 \text{ eV} + 2 \left( \frac{1}{2} p^2 (0.227472 \text{ eV}) \right) \\
&= -p^2 35.32227 \text{ eV} - p^3 0.812025 \text{ eV}
\end{aligned} \tag{13.30}$$

The bond dissociation energy,  $E_D$ , is the difference between the total energy of the corresponding hydrogen molecule and  $E_T$

$$E_D = E(H_2(1/p)) - E_T \tag{13.31}$$

5 where  $E(H_2(1/p))$  is given by Eq. (11.241):

$$E(H_2(1/p)) = -p^2 31.351 \text{ eV} - p^3 0.326469 \text{ eV} \tag{13.32}$$

and  $E(D_2(1/p))$  is given by Eq. (11.242):

$$E(D_2(1/p)) = -p^2 31.4345 \text{ eV} - p^3 0.326469 \text{ eV} \tag{13.33}$$

The  $H_3^+$  bond dissociation energy,  $E_D$ , is given by Eqs. (13.31-13.32) and (13.29):

$$\begin{aligned}
E_D &= -p^2 31.351 \text{ eV} - p^3 0.326469 \text{ eV} - E_T \\
10 \quad &= -p^2 31.351 \text{ eV} - p^3 0.326469 \text{ eV} - (-p^2 35.23714 \text{ eV} - p^3 0.812025 \text{ eV}) \\
&= p^2 3.88614 \text{ eV} + p^3 0.485556 \text{ eV}
\end{aligned} \tag{13.34}$$

The  $D_3^+$  bond dissociation energy,  $E_D$ , is given by Eqs. (13.31), (13.33), and (13.30):

$$\begin{aligned}
E_D &= -p^2 31.4345 \text{ eV} - p^3 0.326469 \text{ eV} - E_T \\
&= -p^2 31.4345 \text{ eV} - p^3 0.326469 \text{ eV} - (-p^2 35.32227 \text{ eV} - p^3 0.812025 \text{ eV}) \\
&= p^2 3.88777 \text{ eV} + p^3 0.485556 \text{ eV}
\end{aligned} \tag{13.35}$$

## 15 THE $H_3^+$ MOLECULAR ION

### FORCE BALANCE OF THE $H_3^+$ MOLECULAR ION

The force balance equation for  $H_3^+$  is given by Eq. (13.5) where  $p=1$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.36}$$

20 which has the parametric solution given by Eq. (11.83) when

$$a = a_o \tag{13.37}$$

The semimajor axis,  $a$ , is also given by Eq. (13.7) where  $p=1$ . The internuclear distance,  $2c'$ , which is the distance between the foci is given by Eq. (13.9) where  $p=1$ .

$$2c' = \sqrt{2}a_o \quad (13.38)$$

The semiminor axis is given by Eq. (13.10) where  $p=1$ .

$$5 \quad b = \frac{1}{\sqrt{2}}a_o \quad (13.39)$$

The eccentricity,  $e$ , is given by Eq. (13.11).

$$e = \frac{1}{\sqrt{2}} \quad (13.40)$$

### ENERGIES OF THE $H_3^+$ MOLECULAR ION

10 The energies of  $H_3^+$  are given by Eqs. (13.12-13.15) where  $p=1$

$$V_e = \frac{3}{2} \frac{-2e^2}{8\pi\epsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -101.7538 \text{ eV} \quad (13.41)$$

$$V_p = 3 \frac{e^2}{8\pi\epsilon_o \sqrt{a^2 - b^2}} = 57.7245 \text{ eV} \quad (13.42)$$

$$T = \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 33.9179 \text{ eV} \quad (13.43)$$

The energy,  $V_m$ , of the magnetic force is

$$15 \quad V_m = \frac{3}{2} \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -25.4384 \text{ eV} \quad (13.44)$$

The Doppler terms,  $\bar{E}_{osc}(H_3^+(1/p))$  and  $\bar{E}_{osc}(D_3^+(1/p))$  are given by Eqs. (13.25) and (13.26), respectively, where  $p=1$

$$\begin{aligned} \bar{E}_{osc}(H_2^+) &= 2(\bar{E}_D + \bar{E}_{Kvib}) \\ &= 2\left(-0.406013 \text{ eV} + \frac{1}{2}(0.312605 \text{ eV})\right) \\ &= -0.499420 \text{ eV} \end{aligned} \quad (13.45)$$

$$\begin{aligned} \bar{E}_{osc}(D_2) &= 2\left(-0.406013 \text{ eV} + \frac{1}{2}(0.227472 \text{ eV})\right) \\ &= -0.584553 \text{ eV} \end{aligned} \quad (13.46)$$

20 The total energy,  $E_T$ , for  $H_3^+$  given by Eqs. (13.27-13.29) is

$$\begin{aligned}
 E_T &= - \left\{ \frac{e^2}{8\pi\epsilon_0 a_0} \left[ \left( 3\sqrt{2} - \sqrt{2} + \frac{3\sqrt{2}}{4} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - 3\sqrt{2} \right] \left[ 1 + 2 \sqrt{\frac{2\hbar \sqrt{\frac{3}{2} \frac{e^2}{4\pi\epsilon_0 a_0^3}}}{m_e c^2}} \right] - 2 \left( \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \right\} \\
 &= -35.54975 - 2(0.406013 \text{ eV}) + 2 \left( \frac{1}{2} (0.31260516 \text{ eV}) \right) \\
 &= -36.049167 \text{ eV}
 \end{aligned} \tag{13.47}$$

From Eqs. (13.27-13.28) and (13.30), the total energy,  $E_T$ , for  $D_3^+$  is

$$\begin{aligned}
 E_T &= -35.54975 - 2(0.406013 \text{ eV}) + 2 \left( \frac{1}{2} (0.227472 \text{ eV}) \right) \\
 &= -36.134300 \text{ eV}
 \end{aligned} \tag{13.48}$$

- 5 The bond dissociation energy,  $E_D$ , is the difference between the total energy of  $H_2$  or  $D_2$  and  $E_T$ . The  $H_3^+$  molecular bond dissociation energy,  $E_D$ , given by the difference between the experimental total energy of  $H_2$  [5-7]<sup>1</sup> and the total energy of  $H_3^+$  (Eqs. (13.29) where  $p=1$  and (13.47)) is

$$\begin{aligned}
 E_D &= -31.675 \text{ eV} - (-36.049167 \text{ eV}) \\
 &= 4.374167 \text{ eV}
 \end{aligned} \tag{13.49}$$

- 10 The  $H_3^+$  bond dissociation energy,  $E_D$ , given by Eq. (13.34) where  $p=1$  is

$$\begin{aligned}
 E_D &= 3.88614 \text{ eV} + 0.485556 \text{ eV} \\
 &= 4.37170 \text{ eV}
 \end{aligned} \tag{13.50}$$

The experimental bond dissociation energy of  $H_3^+$  [8] is

$$E_D = 4.373 \text{ eV} \tag{13.51}$$

- The difference between the results of Eqs. (13.49) and (13.50) is within the experimental and propagated errors in the different calculations. The calculated results are based on first principles and given in closed-form equations containing fundamental constants only. The agreement between the experimental and calculated results for the  $H_3^+$  bond dissociation energy is excellent.

<sup>1</sup> The experimental total energy of the hydrogen molecule is given by adding the first (15.42593 eV) [5] and second (16.2494 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the hydrogen atom (13.59844 eV) [6] and the bond energy of  $H_2^+$  (2.651 eV) [7].

The predicted  $D_3^+$  molecular bond dissociation energy,  $E_D$ , given by the difference between the total energy of  $D_3^+$  (Eqs. (13.30) where  $p=1$  and (13.48)) and the experimental total energy of  $D_2$  [9-10]<sup>2</sup> is

$$\begin{aligned} E_D &= -31.76 \text{ eV} - (-36.134300 \text{ eV}) \\ &= 4.374300 \text{ eV} \end{aligned} \quad (13.52)$$

5 The  $D_3^+$  bond dissociation energy,  $E_D$ , given by Eq. (13.35) where  $p=1$  is

$$\begin{aligned} E_D &= 3.88777 \text{ eV} + 0.485556 \text{ eV} \\ &= 4.373331 \text{ eV} \end{aligned} \quad (13.53)$$

The results of the determination of bond parameters of  $H_3^+$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and  
10 calculated results is excellent.

## HYDROXYL RADICAL (OH)

The water molecule can be solved by first considering the solution of the hydroxyl radical which is formed by the reaction of a hydrogen atom and an oxygen atom:



The hydroxyl radical  $OH$  can be solved using the same principles as those used to solve the hydrogen molecule wherein the diatomic molecular orbital (MO) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serves as basis function in linear combination with an oxygen atomic orbital (AO) to form the MO of  $OH$ .

20 The MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron angular momentum of  $\hbar$ . A further constraint with the substitution of a heteroatom ( $O$ ) for one of the hydrogen atoms is that the constant energy of the MO must  
25 match the energy of the heteroatom.

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<sup>2</sup> The experimental total energy of the deuterium molecule is given by adding the first (15.466 eV) [9] and second (16.294 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the deuterium atom (13.603 eV) [10] and the bond energy of  $D_2^+$  (2.692 eV) [9].

FORCE BALANCE OF  $OH$ 

$OH$  comprises two spin-paired electrons in a chemical bond between the oxygen atom and the hydrogen atom such that one electron on  $O$  remains unpaired. The  $OH$  radical MO is determined by considering properties of the binding atoms and the boundary constraints. The

5 prolate spheroidal  $H_2$  MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, the  $H$ -atom electron forms a  $H_2$ -type ellipsoidal MO with one of the  $O$ -atom electrons. The  $O$  electron configuration given in the Eight-Electron Atoms section is  $1s^2 2s^2 2p^4$ , and the orbital arrangement is

$$\begin{array}{cccc} & \text{2p state} & & \\ \uparrow & \downarrow & \uparrow & \uparrow \\ \hline & 1 & 0 & -1 \end{array} \quad (13.55)$$

10 corresponding to the ground state  $^3P_2$ .

In determining the central forces for  $O$  in the Radius and Ionization Energy of the Outer Electron of the Oxygen Atom section, it was shown that the energy is minimized with conservation of angular momentum by the cancellation of the orbital angular momentum of a  $p_x$  electron by that of the  $p_y$  electron with the pairing of electron eight to fill the  $p_x$  orbital.

15 Then, the diamagnetic force is given by Eq. (10.156) is that of atomic nitrogen (Eq. (10.136) corresponding to the  $p_z$ -orbital electron (Eq. (10.82) with  $m=0$ ) as the source of diamagnetism with an additional contribution from the uncanceled  $p_x$  electron (Eq. (10.82) with  $m=1$ ). From Eqs. (10.83) and (10.89), the paramagnetic force,  $F_{mag 2}$ , is given by Eq. (10.157) corresponding to the spin-angular-momentum contribution alone of the  $p_x$  electron

20 and the orbital angular momentum of the  $p_z$  electron, respectively. The diamagnetic and paramagnetic forces cancel such that the central force is purely the Coulombic force. This central force is maintained with bond formation such that the energy of the  $O2p$  shell is unchanged. Thus, the angular momentum of each electron of the  $O2p$  shell is conserved with bond formation. The central paramagnetic force due to spin is provided by the spin-

25 pairing force of the  $OH$  MO that has the symmetry of an  $s$  orbital that superimposes with the  $2p$  orbitals such that the corresponding angular momenta of the  $O2p$  orbitals are unchanged.

The  $O2p_y$  electron combines with the  $H1s$  electron to form a molecular orbital. The proton of the  $H$  atom is along the internuclear axis. Due to symmetry, the other  $O$  electrons



are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix IV.) Thus, the energies in the  $OH$  MO involve only the  $O2p_y$  and  $H1s$  electrons and the change in the magnetic energy of the  $O2p_y$  electron with the other  $O$  electrons (Eq. (13.152)) with the formation of the  $OH$  MO. The forces are determined by these energies.

5 As in the case of  $H_2$ , the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $O$  atom for distances shorter than the radius of the  $2p$  shell. Otherwise, the electric field of the other  $O2p$  electrons would be perturbed, and the  $2p$  shell would not be stable. The corresponding increase in energy of  $O$  would not be offset by any energy decrease in the  $OH$  MO based on the distance from the  $O$  nucleus to  
 10 the  $H1s$  electron compared to those of the  $O2p$  electrons. Thus, the MO surface comprises a prolate spheroid at the  $H$  proton that is continuous with the  $2p$  shell at the  $O$  atom. The energy of the prolate spheroid is matched to that of the  $O2p$  shell.

The orbital energy  $E$  for each elliptical cross section of the prolate spheroidal MO is given by the sum of the kinetic  $T$  and potential  $V$  energies.  $E = T + V$  is constant, and the  
 15 closed orbits are those for which  $T < |V|$ , and the open orbits are those for which  $T \geq |V|$ . It can be shown that the time average of the kinetic energy,  $\langle T \rangle$ , for elliptic motion in an inverse-squared field is  $1/2$  that of the time average of the magnitude of the potential energy,  $\langle |V| \rangle$ .  $\langle T \rangle = 1/2 \langle |V| \rangle$  [11]. In the case of an atomic orbital (AO),  $E = T + V$ , and for all points on the AO,  $|E| = T = 1/2 |V|$ . As shown in the Hydrogen-type Molecular Ions section,  
 20 each point or coordinate position on the continuous two-dimensional electron MO defines an infinitesimal mass-density element which moves along an orbit comprising an elliptic plane cross section of the spheroidal MO through the foci. The motion is such that eccentric angle,  $\theta$ , changes at a constant rate at each point. That is  $\theta = \omega t$  at time  $t$  where  $\omega$  is a constant, and

$$25 \quad r(t) = \mathbf{i}a \cos \omega t + \mathbf{j}b \sin \omega t \quad (13.56)$$

Consider the boundary condition that the MO of  $OH$  comprises a linear combination of an oxygen AO and a  $H_2$ -type ellipsoidal MO. The charge density of  $H_2$ -type ellipsoidal MO given by Eq. (13.4) maintains that the surface is an equipotential; however, the potential and kinetic energy of a point on the surface changes as it orbits the central field. The potential  
 30 energy is a maximum and the kinetic energy is a minimum at the semimajor axis, and the reverse occurs at the semiminor axis. Since the time average of the kinetic energy,  $\langle T \rangle$ , for

elliptic motion in an inverse-squared field is  $1/2$  that of the time average of the magnitude of the potential energy, by symmetry, the  $\langle T \rangle = 1/2 \langle |V| \rangle$  condition holds for  $1/2$  of the  $H_2$ -type ellipsoidal MO having the  $H$  focus and ending at the plane defined by the semiminor axes. The  $O$  nucleus comprises the other focus of the  $OH$  MO. The  $O2p$  AO obeys the  
 5 energy relationship for all points. Thus, the linear combination of the  $H_2$ -type ellipsoidal MO with the  $O2p$  AO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the  $O2p$  AO in order to match the energy relationships. Thus, the  $OH$  MO must comprise 75% of a  $H_2$ -type ellipsoidal MO ( $1/2 + 25\%$ ) and an oxygen AO:

$$10 \quad 1 O2p_y \text{ AO} + 0.75 H_2 \text{ MO} \rightarrow OH \text{ MO} \quad (13.57)$$

The force balance of the  $OH$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.57). The force constant  $k$  of a  $H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by  
 15 Eq. (11.65):

$$k = \frac{2e^2}{4\pi\epsilon_0} \quad (13.58)$$

Since the  $H_2$ -type ellipsoidal MO comprises 75% of the  $OH$  MO, the electron charge density in Eq. (13.58) is given by  $-0.75e$ . Thus,  $k'$  of the  $H_2$ -type-ellipsoidal-MO component of the  $OH$  MO is

$$20 \quad k' = \frac{(0.75)2e^2}{4\pi\epsilon_0} \quad (13.59)$$

$L$  for the electron equals  $\hbar$ ; thus, the distance from the origin of the  $OH$  MO to each focus  $c'$  is given by Eqs. (11.79) and (13.59):

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 1.5a}} = \sqrt{\frac{2aa_0}{3}} \quad (13.60)$$

The internuclear distance from Eq. (13.60) is

$$25 \quad 2c' = 2\sqrt{\frac{2aa_0}{3}} \quad (13.61)$$

The length of the semiminor axis of the prolate spheroidal  $OH$  MO  $b = c$  given by Eq. (11.80) is

$$b = \sqrt{a^2 - c'^2} \quad (13.62)$$

The eccentricity,  $e$ , is

$$e = \frac{c'}{a} \quad (13.63)$$

Then, the solution of the semimajor axis  $a$  allows for the solution of the other axes of the  
5 prolate spheroidal and eccentricity of the  $OH$  MO.

The general equation of the ellipsoidal MO having semiprincipal axes  $a, b, c$  given  
by

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \quad (13.64)$$

is also completely determined by the total energy  $E$  given by Eq. (11.18):

$$10 \quad r = \frac{m \frac{L^2}{m^2} k^{-1}}{1 + \left( 1 + 2Em \frac{L^2}{m^2} k^{-2} \right)^{1/2} \cos \theta} \quad (13.65)$$

The energy of the oxygen  $2p$  shell is the negative of the ionization energy of the oxygen  
atom given by Eq. (10.163). Experimentally, the energy is [12]

$$E(2p \text{ shell}) = -E(\text{ionization}; O) = -13.6181 \text{ eV} \quad (13.66)$$

Since the prolate spheroidal MO transitions to the  $O$  AO, the energy  $E$  in Eq. (13.66) adds  
15 to that of the  $H_2$ -type ellipsoidal MO to give the total energy of the  $OH$  MO. From the  
energy equation and the relationship between the axes given by Eqs. (13.60-13.63), the  
dimensions of the  $OH$  MO are solved.

The energy components derived previously for the hydrogen molecule, Eqs. (11.207-  
11.212), apply in the case of the  $H_2$ -type ellipsoidal MO. As in the case of the energies of  
20  $H_3^+(1/p)$  given by Eqs. (13.12-13.16), each energy component of the  $H_2$ -type ellipsoidal  
MO is the total for the two equivalent electrons with the exception that the total charge and  
energies of the two electrons is normalized by the percentage composition given by Eq.  
(13.57):

$$V_e = \left( \frac{3}{4} \right) \frac{-2e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \quad (13.67)$$

$$25 \quad V_p = \frac{e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \quad (13.68)$$

$$T = \left(\frac{3}{4}\right) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \quad (13.69)$$

$$V_m = \left(\frac{3}{4}\right) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \quad (13.70)$$

$$E_T = V_e + T + V_m + V_p \quad (13.71)$$

$$E_T = -\frac{e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \left[ \left( \frac{3}{2} - \frac{3}{4} \frac{a_0}{a} + \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} - 1 \right] \quad (13.72)$$

$$5 \quad E_T = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \quad (13.73)$$

Since the prolate spheroidal MO transitions to the  $O$  AO and the energy of the  $O2p$  shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.66), the total energy  $E_T(OH)$  of the  $OH$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $O$  AO and the  $H_2$ -type ellipsoidal MO that forms the  $OH$  MO as given by Eq. (13.57):

$$\begin{aligned} E_T(OH) &= E_T + E(2p \text{ shell}) \\ &= E_T - E(\text{ionization}; O) \\ &= -\frac{e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 13.6181 \text{ eV} \end{aligned} \quad (13.74)$$

To match the boundary condition that the total energy of the entire the  $H_2$ -type ellipsoidal MO is given by Eq. (11.212):

$$E_T(H_2) = -\frac{e^2}{8\pi\epsilon_0 a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} - \sqrt{2} \right] = -31.63536831 \text{ eV} \quad (13.75)$$

15  $E_T(OH)$  given by Eq. (13.74) is set equal to Eq. (13.75):

$$\begin{aligned} E_T(OH) &= -\frac{e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 13.6181 \text{ eV} = -31.63536831 \text{ eV} \\ &\quad (13.76) \end{aligned}$$

From the energy relationship given by Eq. (13.76) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $OH$  MO can be solved.

20 Substitution of Eq. (13.60) into Eq. (13.76) gives

$$\frac{e^2}{8\pi\epsilon_0\sqrt{\frac{2aa_0}{3}}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right] = e18.01726831 \quad (13.77)$$

The most convenient way to solve Eq. (13.77) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.26430a_0 = 6.69039 \times 10^{-11} \text{ m} \quad (13.78)$$

5 Substitution of Eq. (13.78) into Eq. (13.60) gives

$$c' = 0.91808a_0 = 4.85826 \times 10^{-11} \text{ m} \quad (13.79)$$

The internuclear distance given by multiplying Eq. (13.79) by two is

$$2c' = 1.83616a_0 = 9.71651 \times 10^{-11} \text{ m} \quad (13.80)$$

The experimental bond distance is [13]

$$10 \quad 2c' = 9.71 \times 10^{-11} \text{ m} \quad (13.81)$$

Substitution of Eqs. (13.78-13.79) into Eq. (13.62) gives

$$b = c = 0.86925a_0 = 4.59985 \times 10^{-11} \text{ m} \quad (13.82)$$

Substitution of Eqs. (13.78-13.79) into Eq. (13.63) gives

$$e = 0.72615 \quad (13.83)$$

15 The nucleus of the  $H$  atom and the nucleus of the  $O$  atom comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $O2p_y$  AO can be determined from the polar equation of the ellipse (Eq. (11.10)):

$$r = r_0 \frac{1+e}{1+e \cos \theta'} \quad (13.84)$$

20 The radius of the  $O2p_y$  AO given by Eq. (10.162) is  $r_s = a_0$ , and the polar radial coordinate of the ellipse and the radius of the  $O2p_y$  AO are equal at the point of intersection. Thus, Eq. (13.84) becomes

$$a_0 = (a - c') \frac{1 + \frac{c'}{a}}{1 + \frac{c'}{a} \cos \theta'} \quad (13.85)$$

such that the polar angle  $\theta'$  is given by

$$\theta' = \cos^{-1} \left[ \frac{a}{c'} \left( (a - c') \frac{1 + \frac{c'}{a}}{a_0} - 1 \right) \right] \quad (13.86)$$

Substitution of Eqs. (13.78-13.79) into Eq. (13.86) gives

$$\theta' = 123.65^\circ \quad (13.87)$$

Then, the angle  $\theta_{O2p_yAO}$  the radial vector of the  $O2p_y$  AO makes with the internuclear axis is

$$\theta_{O2p_yAO} = 180^\circ - 123.65^\circ = 56.35^\circ \quad (13.88)$$

as shown in Figure 7.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the radial vector obeys the following relationship:

$$a_0 \sin \theta_{O2p_yAO} = b \sin \theta_{H_2MO} \quad (13.89)$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{a_0 \sin 56.35^\circ}{b} \quad (13.90)$$

with the use of Eq. (13.88). Substitution of Eq. (13.82) into Eq. (13.90) gives

$$\theta_{H_2MO} = 73.27^\circ \quad (13.91)$$

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a \cos \theta_{H_2MO} \quad (13.92)$$

Substitution of Eqs. (13.78) and (13.91) into Eq. (13.92) gives

$$d_{H_2MO} = 0.36397a_0 = 1.92606 \times 10^{-11} \text{ m} \quad (13.93)$$

The distance  $d_{O2pAO}$  along the internuclear axis from the origin of the  $O$  atom to the point of intersection of the orbitals is given by

$$d_{O2pAO} = c' - d_{H_2MO} \quad (13.94)$$

Substitution of Eqs. (13.79) and (13.93) into Eq. (13.94) gives

$$d_{O2pAO} = 0.55411a_0 = 2.93220 \times 10^{-11} \text{ m} \quad (13.95)$$

As shown in Eq. (13.57), in addition to the  $p$ -orbital charge-density modulation, the uniform charge-density in the  $p_y$  orbital is increased by a factor of 0.25 and the  $H$ -atom density is decreased by a factor of 0.25. The internuclear axis of the  $O-H$  bond is perpendicular to the bonding  $p_y$  orbital. Using the orbital composition of  $OH$  (Eq. (13.57)), the radii of  $O1s = 0.12739a_0$  (Eq. (10.51)),  $O2s = 0.59020a_0$  (Eq. (10.62)), and  $O2p = a_0$  (Eq. (10.162)) shells, and the parameters of the  $OH$  MO given by Eqs. (13.3-13.4), (13.78-13.80), (13.82-13.83), and (13.87-13.95), the dimensional diagram and charge-density of the  $OH$  MO comprising the linear combination of the  $H_2$ -type ellipsoidal MO and the  $O$  AO according to Eq. (13.57) are shown in Figures 7 and 8, respectively.

10

### ENERGIES OF $OH$

The energies of  $OH$  given by the substitution of the semiprincipal axes (Eqs. (13.78-13.80) and (13.82)) into the energy equations (Eqs. (13.67-13.73)) are

$$V_e = \left(\frac{3}{4}\right) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -40.92709 \text{ eV} \quad (13.96)$$

15

$$V_p = \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 14.81988 \text{ eV} \quad (13.97)$$

$$T = \left(\frac{3}{4}\right) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 16.18567 \text{ eV} \quad (13.98)$$

$$V_m = \left(\frac{3}{4}\right) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -8.09284 \text{ eV} \quad (13.99)$$

$$E_T(OH) = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 13.6181 \text{ eV} = -31.63247 \text{ eV} \quad (13.100)$$

where  $E_T(OH)$  is given by Eq. (13.74) which is reiteratively matched to Eq. (13.75) within five-significant-figure round-off error.

### VIBRATION AND ROTATION OF $OH$

The vibrational energy of  $OH$  may be solved in the same manner as that of hydrogen-type molecular ions and hydrogen molecules given in the Vibration of Hydrogen-type Molecular Ions section, and the Vibration of Hydrogen-type Molecules section, respectively, except that the orbital composition and the requirement that the  $O2p$  shell remain at the same energy and

radius in the  $OH$  MO as it is in the  $O$  atom must be considered. Each  $p$ -orbital comprises the sum of a constant function and a spherical harmonic function as given by Eq. (1.65). In addition to the  $p$ -orbital charge-density modulation, the uniform charge-density in  $p_y$  orbital is increased by a factor of 0.25, and the  $H$ -atom electron density is decreased by a factor of 5 0.25. The force between the electron density of the  $H_2$ -type ellipsoidal MO and the nuclei determines the vibrational energy. With the radius of the orbit at the oxygen atom fixed at

$$r_s = a_0 \quad (13.101)$$

according to Eq. (10.162), the central-force terms for the reentrant orbit between the electron density and the nuclei of the  $H_2$ -type ellipsoidal MO are given by Eqs. (11.213-11.214), 10 except that the corresponding charge of  $-0.75e$  replaces the charge of  $-e$  of Eqs. (11.213-11.214). Furthermore, due to condition that the  $O2p$  shell remain at the same energy and radius in the  $OH$  MO as it is in the  $O$  atom, the oscillation of  $H_2$ -type ellipsoidal is along the semiminor axis with the apsidal angle of Eq. (11.140) given by  $\psi = \pi$ . Thus, the semimajor axis  $a$  of Eqs. (11.213-11.214) is replaced by the semiminor axis  $b$ :

$$15 \quad f(b) = -\frac{0.75e^2}{8\pi\epsilon_0 b^2} \quad (13.102)$$

and

$$f'(b) = \frac{0.75e^2}{4\pi\epsilon_0 b^3} \quad (13.103)$$

Here, the force factor of 0.75 is equal to the equivalent term of Eq. (13.59). As the  $H_2$ -type ellipsoidal oscillates along  $b$ , the internuclear distance changes  $180^\circ$  out of phase. Thus, the 20 distance for the reactive nuclear-repulsive terms is given by internuclear distance  $2c'$  (Eq. (13.80)). Similar to that of Eqs. (11.215-11.216), the contribution from the repulsive force between the two nuclei is

$$f(2c') = \frac{e^2}{8\pi\epsilon_0 (2c')^2} \quad (13.104)$$

and

$$25 \quad f'(2c') = -\frac{e^2}{4\pi\epsilon_0 (2c')^3} \quad (13.105)$$

Thus, from Eqs. (11.136), (11.213-11.217), and (13.102-13.105), the angular frequency of the oscillation is



$$\begin{aligned}
 \omega &= \sqrt{\frac{\frac{0.75e^2}{8\pi\epsilon_0 b^3} - \frac{e^2}{8\pi\epsilon_0 (2c')^3}}{\mu}} \\
 &= \sqrt{\frac{\frac{0.75e^2}{8\pi\epsilon_0 (0.86925a_0)^3} - \frac{e^2}{8\pi\epsilon_0 (1.83616a_0)^3}}{\frac{16}{17}m_p}} \\
 &= 6.96269 \times 10^{14} \text{ rad/s}
 \end{aligned} \tag{13.106}$$

where  $b$  is given by Eq. (13.82),  $2c'$  is given by Eq. (13.80), and the reduced mass of  $^{16}\text{OH}$  is given by:

$$\mu_{^{16}\text{OH}} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1)(16)}{1+16} m_p \tag{13.107}$$

5 where  $m_p$  is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency,  $\omega(0)$ , for  $^{16}\text{OH}$  given by Eqs. (11.136), (11.148), and (13.106) is

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{763.18 \text{ Nm}^{-1}}{\mu}} = 6.96269 \times 10^{14} \text{ radians/s} \tag{13.108}$$

10 where the reduced nuclear mass of  $^{16}\text{OH}$  is given by Eq.(13.107) and the spring constant,  $k(0)$ , given by Eqs. (11.136) and (13.106) is

$$k(0) = 763.18 \text{ Nm}^{-1} \tag{13.109}$$

The  $^{16}\text{OH}$  transition-state vibrational energy,  $E_{\text{vib}}(0)$ , given by Planck's equation (Eq. (11.127)) is:

$$15 \quad E_{\text{vib}}(0) = \hbar\omega = \hbar 6.96269 \times 10^{14} \text{ rad/s} = 0.4583 \text{ eV} = 3696.38 \text{ cm}^{-1} \tag{13.110}$$

Zero-order or zero-point vibration is not physical and is not observed experimentally as discussed in the Diatomic Molecular Vibration section; yet, there is a term  $\omega_e$  of the old point-particle-probability-wave-mechanics that can be compared to  $E_{\text{vib}}(0)$ . From Herzberg [14],  $\omega_e$ , from the experimental curve fit of the vibrational energies of  $^{16}\text{OH}$  is

$$20 \quad \omega_e = 3735.21 \text{ cm}^{-1} \tag{13.111}$$

As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and

expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods. The energy  $\tilde{\nu}_\nu$  of state  $\nu$  is

$$5 \quad \tilde{\nu}_\nu = \nu\omega_0 - \nu(\nu-1)\omega_0x_0, \quad \nu = 0, 1, 2, 3... \quad (13.112)$$

where

$$\omega_0x_0 = \frac{hc\omega_0^2}{4D_0} \quad (13.113)$$

$\omega_0$  is the frequency of the  $\nu = 1 \rightarrow \nu = 0$  transition, and  $D_0$  is the bond dissociation energy given by Eq. (13.162). From Eq. (13.112),  $\omega_0$  is given by

$$10 \quad \omega_0 = E_{vib}(0) - 2\omega_0x_0 \quad (13.114)$$

Substitution of Eq. (13.113) into Eq. (13.114) gives

$$\omega_0 = E_{vib}(0) - 2\frac{hc\omega_0^2}{4D_0} \quad (13.115)$$

Eq. (13.115) can be expressed as

$$\omega_0^2 + \frac{2D_0}{hc}\omega_0 - \frac{2D_0}{hc}E_{vib}(0) = 0 \quad (13.116)$$

15 which can be solved by the quadratic formula:

$$\omega_0 = \frac{-\frac{2D_0}{hc} \pm \sqrt{\left(\frac{2D_0}{hc}\right)^2 + 4\frac{2D_0}{hc}E_{vib}(0)}}{2} \quad (13.117)$$

Only the positive root is real, physical; thus,

$$\begin{aligned} \omega_0 (cm^{-1}) &= \frac{-\frac{2D_0}{100hc} + \sqrt{\left(\frac{2D_0}{100hc}\right)^2 + 4\frac{2D_0}{100hc}E_{vib}(0)}}{2} \\ &= \frac{-\frac{2e(4.4104 eV)}{100hc} + \sqrt{\left(\frac{2e(4.4104 eV)}{100hc}\right)^2 + 4\frac{2e(4.4104 eV)}{100hc}(3696.37 cm^{-1})}}{2} \\ &= 3522.02 cm^{-1} \end{aligned} \quad (13.118)$$

where  $E_{vib}(0)$  is given by Eq. (13.110) and  $D_0$  is given by Eq. (13.156). The corresponding  $^{16}OH$   $\nu = 1 \rightarrow \nu = 0$  vibrational energy,  $E_{vib}(1)$ , in electron volts is:

$$E_{vib}(1) = 0.43666 \text{ eV} \quad (13.119)$$

The experimental vibrational energy of  $^{16}OH$  is [16-17]

$$5 \quad E_{vib}(1) = 0.4424 \text{ eV} \quad (3568 \text{ cm}^{-1}) \quad (13.120)$$

Using Eqs. (13.118-13.119) with Eq. (13.113), the anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{16}OH$  is

$$\omega_0 x_0 = \frac{100hc \left( 8.06573 \times 10^3 \frac{\text{cm}^{-1}}{\text{eV}} 0.43666 \text{ eV} \right)^2}{4e(4.4104 \text{ eV})} \text{cm}^{-1} = 87.18 \text{ cm}^{-1} \quad (13.121)$$

The experimental anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{16}OH$  [14] is

$$10 \quad \omega_0 x_0 = 82.81 \text{ cm}^{-1} \quad (13.122)$$

The vibrational energies of successive states are given by Eqs. (13.110), (13.112), and (13.121).

Using the reduced nuclear mass of  $^{16}OD$  given by

$$\mu_{^{16}OD} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(2)(16)}{2 + 16} m_p \quad (13.123)$$

15 where  $m_p$  is the proton mass, the corresponding parameters for deuterated hydroxyl radical  $^{16}OD$  (Eqs. (13.102-13.121) and (13.162)) are

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{763.18 \text{ Nm}^{-1}}{\mu}} = 5.06610 \times 10^{14} \text{ radians/s} \quad (13.124)$$

$$k(0) = 763.18 \text{ Nm}^{-1} \quad (13.125)$$

$$E_{vib}(0) = \hbar\omega = \hbar 5.06610 \times 10^{14} \text{ rad/s} = 0.33346 \text{ eV} = 2689.51 \text{ cm}^{-1} \quad (13.126)$$

$$\begin{aligned}
 \omega_0 (cm^{-1}) &= \frac{-\frac{2D_0}{100hc} + \sqrt{\left(\frac{2D_0}{100hc}\right)^2 + 4\frac{2D_0}{100hc}E_{vib}(0)}}{2} \\
 &= \frac{-\frac{2e(4.4687 eV)}{100hc} + \sqrt{\left(\frac{2e(4.4687 eV)}{100hc}\right)^2 + 4\frac{2e(4.4687 eV)}{100hc}(2689.51 cm^{-1})}}{2} \\
 &= 2596.02 cm^{-1}
 \end{aligned}
 \tag{13.127}$$

$$E_{vib}(1) = 0.3219 eV \tag{13.128}$$

$$\omega_0 x_0 = \frac{100hc \left( 8.06573 \times 10^3 \frac{cm^{-1}}{eV} 0.3219 eV \right)^2}{4e(4.4687 eV)} cm^{-1} = 46.75 cm^{-1} \tag{13.129}$$

From Herzberg [14],  $\omega_e$ , from the experimental curve fit of the vibrational energies of  $^{16}OD$  is

$$\omega_e = 2720.9 cm^{-1} \tag{13.130}$$

The experimental vibrational energy of  $^{16}OD$  is [16-17]

$$E_{vib}(1) = 0.3263 eV \quad (2632.1 cm^{-1}) \tag{13.131}$$

and the experimental anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{16}OD$  [14] is

$$\omega_0 x_0 = 44.2 cm^{-1} \tag{13.132}$$

which match the predictions given by Eqs. (13.126), (13.127-13.128), and (13.129), respectively.

The  $B_e$  rotational parameters for  $^{16}OH$  and  $^{16}OD$  are given by Eq. (12.65):

$$B_e = \frac{\hbar^2}{2I_e hc} \tag{13.133}$$

where

$$I = \mu r^2 \tag{13.134}$$

Using the internuclear distance,  $r = 2c'$ , and reduced mass of  $^{16}OH$  given by Eqs. (13.80) and (13.107), respectively, the corresponding  $B_e$  is

$$B_e = 18.835 cm^{-1} \tag{13.135}$$

The experimental  $B_e$  rotational parameter of  $^{16}OH$  is [14]

$$B_e = 18.871 \text{ cm}^{-1} \quad (13.136)$$

Using the internuclear distance,  $r = 2c'$ , and reduced mass of  $^{16}\text{OD}$  given by Eqs. (13.80) and (13.123), respectively, the corresponding  $B_e$  is

$$B_e = 9.971 \text{ cm}^{-1} \quad (13.137)$$

5 The experimental  $B_e$  rotational parameter of  $^{16}\text{OD}$  is [14]

$$B_e = 10.01 \text{ cm}^{-1} \quad (13.138)$$

### THE DOPPLER ENERGY TERMS OF $^{16}\text{OH}$ AND $^{16}\text{OD}$

The radiation reaction force in the case of the vibration of  $^{16}\text{OH}$  in the transition state  
10 corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) and Eq. (13.22) that is  
dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient  
vibration is derived from the corresponding central forces. Following the same consideration  
as those used to derive Eqs. (13.102-13.103) and Eqs. (11.231-11.232), the central force  
terms between the electron density and the nuclei of  $^{16}\text{OH}$  MO with the radius of the orbit at  
15 the oxygen atom fixed at

$$r_8 = a_0 \quad (13.139)$$

according to Eq. (10.162) are

$$f(b) = -\frac{0.75e^2}{4\pi\epsilon_0 b^2} \quad (13.140)$$

and

$$20 \quad f'(b) = \frac{(0.75)2e^2}{4\pi\epsilon_0 b^3} \quad (13.141)$$

wherein the oscillation of  $H_2$ -type ellipsoidal MO is along the semiminor axis  $b$  with the  
apsidal angle of Eq. (11.140) given by  $\psi = \pi$  due to condition that the  $O2p$  shell remain at  
the same energy and radius in the  $\text{OH}$  MO as it is in the  $\text{O}$  atom. Thus, using Eqs. (11.136)  
and (13.140-13.141), the angular frequency of this oscillation is

$$25 \quad \omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 4.41776 \times 10^{16} \text{ rad/s} \quad (13.142)$$

The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

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$$\bar{E}_K = \hbar\omega = \hbar 4.41776 \times 10^{16} \text{ rad/s} = 29.07844 \text{ eV} \quad (13.143)$$

In Eq. (11.181), substitution of the total energy of  $OH$ ,  $E_T(OH)$ , (Eq. (13.76)) for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.143) for  $\bar{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit.

$$5 \quad \bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(29.07844 \text{ eV})}{m_e c^2}} = -0.33749 \text{ eV} \quad (13.144)$$

The total energy of  $OH$  is decreased by  $\bar{E}_D$ .

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [4]. Thus, the average  
 10 kinetic energy of vibration corresponding to the Doppler energy of the electrons,  $\bar{E}_{Kvib}$ , is 1/2 of the vibrational energy of  $OH$  given by Eq. (13.120). The decrease in the energy of the  $OH$  due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  and  $\bar{E}_{Kvib}$ . Using Eq. (13.144) and the experimental  $^{16}OH$   $\omega_e$  of  
 15  $3735.21 \text{ cm}^{-1}$  ( $0.463111 \text{ eV}$ ) [16-17] gives

$$\bar{E}_{osc}(^{16}OH) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.145)$$

$$\bar{E}_{osc}(^{16}OH) = -0.33749 \text{ eV} + \frac{1}{2} (0.463111 \text{ eV}) = -0.10594 \text{ eV} \quad (13.146)$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies,  $\bar{E}_K$ , are the same independent of the isotope of hydrogen, but the vibrational  
 20 energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies per bond. Using Eq. (13.144), Eqs. (13.145-13.146), and the experimental  $^{16}OD$   $\omega_e$  of  $2720.9 \text{ cm}^{-1}$  ( $0.33735 \text{ eV}$ ) [16-17], the corresponding  $\bar{E}_{osc}(^{16}OD)$  is

$$\bar{E}_{osc}(^{16}OD) = -0.33749 \text{ eV} + \frac{1}{2} (0.33735 \text{ eV}) = -0.16881 \text{ eV} \quad (13.147)$$

TOTAL AND BOND ENERGIES OF  $^{16}\text{OH}$  AND  $^{16}\text{OD}$  RADICALS

$E_{T+osc}(^{16}\text{OH})$ , the total energy of the  $^{16}\text{OH}$  radical including the Doppler term, is given by the sum of  $E_T(\text{OH})$  (Eq. (13.76)) and  $\bar{E}_{osc}(^{16}\text{OH})$  given by Eqs. (13.142-13.146):

$$\begin{aligned} E_{T+osc}(^{16}\text{OH}) &= V_e + T + V_m + V_p + E(2p \text{ shell}) + \bar{E}_{osc}(^{16}\text{OH}) \\ &= E_T(\text{OH}) + \bar{E}_{osc}(^{16}\text{OH}) \end{aligned} \quad (13.148)$$

$$\begin{aligned} E_{T+osc}(^{16}\text{OH}) &= \left\{ \frac{-e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 13.6181 \text{ eV} \right\} \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{3}{4} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2}} \right] + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \\ &= -31.63537 \text{ eV} - 0.33749 \text{ eV} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \end{aligned} \quad (13.149)$$

From Eqs. (13.145-13.146) and (13.148-13.149), the total energy of  $^{16}\text{OH}$  is

$$\begin{aligned} E_{T+osc}(^{16}\text{OH}) &= -31.63537 \text{ eV} + \bar{E}_{osc}(^{16}\text{OH}) \\ &= -31.63537 \text{ eV} - 0.33749 \text{ eV} + \frac{1}{2} (0.463111 \text{ eV}) \\ &= -31.74130 \text{ eV} \end{aligned} \quad (13.150)$$

where the experimental  $\omega_e$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.  $E_{T+osc}(^{16}\text{OD})$ , the total energy of  $^{16}\text{OD}$  including the Doppler term, is given by the sum of  $E_T(\text{OD}) = E_T(\text{OH})$  (Eq. (13.76)) and  $\bar{E}_{osc}(^{16}\text{OD})$  given by Eq. (13.147):

$$\begin{aligned} E_{T+osc}(^{16}\text{OD}) &= -31.63537 \text{ eV} + \bar{E}_{osc}(^{16}\text{OD}) \\ &= -31.63537 \text{ eV} - 0.33749 \text{ eV} + \frac{1}{2} (0.33735 \text{ eV}) \\ &= -31.80418 \text{ eV} \end{aligned} \quad (13.151)$$

where the experimental  $\omega_e$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term. The dissociation of the bond of the hydroxyl radical forms a free hydrogen atom with one unpaired electron and an oxygen atom with two unpaired electrons as shown in Eq. (13.55) which interact to stabilize the atom as shown by Eq. (10.161-10.162). The lowering of the energy of the reactants decreases the bond energy. Thus, the total energy of oxygen is reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.101):

$$E(\text{magnetic}) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 a_0^3} = \frac{8\pi\mu_0 \mu_B^2}{a_0^3} = 0.114411 \text{ eV} \quad (13.152)$$

The corresponding bond dissociation energy,  $E_D$ , is given by the sum of the total energies of the oxygen atom and the corresponding hydrogen atom minus the sum of  $E_{T+osc}({}^{16}\text{OH})$  and  $E(\text{magnetic})$ :

$$5 \quad E_D = E({}^{16}\text{O}) + E(\text{H}) - E_{T+osc}({}^{16}\text{OH}) - E(\text{magnetic}) \quad (13.153)$$

$E({}^{16}\text{O})$  is given by Eq. (13.66),  $E_D(\text{H})$  [18] is

$$E(\text{H}) = -13.59844 \text{ eV} \quad (13.154)$$

and  $E_D(\text{D})$  [19] is

$$E(\text{D}) = -13.603 \text{ eV} \quad (13.155)$$

10 The  ${}^{16}\text{OH}$  bond dissociation energy,  $E_D({}^{16}\text{OH})$ , is given by Eqs. (13.150) and (13.152-13.155):

$$\begin{aligned} E_D({}^{16}\text{OH}) &= -(13.6181 \text{ eV} + 13.59844 \text{ eV}) - (E(\text{magnetic}) + E_{T+osc}({}^{16}\text{OH})) \\ &= -27.21654 \text{ eV} - (0.114411 \text{ eV} - 31.74130 \text{ eV}) \\ &= 4.4104 \text{ eV} \end{aligned} \quad (13.156)$$

The experimental  ${}^{16}\text{OH}$  bond dissociation energy is [20]

$$E_D({}^{16}\text{OH}) = 4.41174 \text{ eV} \quad (13.157)$$

15 The  ${}^{16}\text{OD}$  bond dissociation energy,  $E_D({}^{16}\text{OD})$ , is given by Eqs. (13.151-13.153):

$$\begin{aligned} E_D({}^{16}\text{OD}) &= -(13.6181 \text{ eV} + 13.603 \text{ eV}) - (E(\text{magnetic}) + E_{T+osc}({}^{16}\text{OD})) \\ &= -27.2211 \text{ eV} - (0.114411 \text{ eV} - 31.804183 \text{ eV}) \\ &= 4.4687 \text{ eV} \end{aligned} \quad (13.158)$$

The experimental  ${}^{16}\text{OD}$  bond dissociation energy is [21-22]

$$E_D({}^{16}\text{OD}) = 4.454 \text{ eV} \quad (13.159)$$

The results of the determination of bond parameters of  $\text{OH}$  and  $\text{OD}$  are given in  
20 Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.



## WATER MOLECULE ( $H_2O$ )

The water molecule  $H_2O$  is formed by the reaction of a hydrogen atom with a hydroxyl radical:



- 5 The water molecule can be solved using the same principles as those used to solve the hydrogen molecule,  $H_2^+$ , and  $OH$  wherein the diatomic molecular orbital (MO) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serves as basis function in a linear combination with an oxygen atomic orbital (AO) to form the MO of  $H_2O$ . The solution is very similar to that of  $OH$  except that there are two  $OH$
- 10 bonds in water.

## FORCE BALANCE OF $H_2O$

$H_2O$  comprises two chemical bonds between oxygen and hydrogen. Each  $O-H$  bond comprises two spin-paired electrons with one from an initially unpaired electron of the

15 oxygen atom and the other from the hydrogen atom. The  $H_2O$  MO is determined by considering properties of the binding atoms and the boundary constraints. The  $H_2$  prolate spheroidal MO satisfies the boundary constraints as shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section; thus, each  $H$ -atom electron forms a  $H_2$ -type ellipsoidal MO with one of the initially unpaired  $O$ -atom electrons. The initial  $O$  electron

20 configuration given in the Eight-Electron Atoms section is  $1s^2 2s^2 2p^4$ , and the orbital arrangement is given by Eqs. (10.154) and Eq. (13.55).

As shown in the case of  $OH$  in the Force Balance of  $OH$  section, the forces that determine the radius and the energy of the  $O2p$  shell are unchanged with bond formation. Thus, the angular momentum of each electron of the  $O2p$  is conserved with bond formation.

25 The central paramagnetic force due to spin of each  $O-H$  bond is provided by the spin-paring force of the  $H_2O$  MO that has the symmetry of an  $s$  orbital that superimposes with the  $O2p$  orbitals such that the corresponding angular momenta are unchanged.

Each of the  $O2p_z$  and  $O2p_x$  electron combines with a  $H1s$  electron to form a molecular orbital. The proton of the  $H$  atom is along the internuclear axis. Due to

30 symmetry, the other  $O$  electrons are equivalent to point charges at the origin. (See Eqs. (19-

38) of Appendix IV.) Thus, the energies in the  $H_2O$  MO involve only each  $O2p$  and each  $H1s$  electron with the formation of each  $O-H$  bond. The forces are determined by these energies.

As in the case of  $H_2$ , each of two  $O-H$ -bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the  $O$  atom for distances shorter than the radius of the  $2p$  shell. Otherwise, the electric field of the other  $O2p$  electrons would be perturbed, and the  $2p$  shell would not be stable. The corresponding increase in energy of  $O$  would not be offset by any energy decrease in the  $O-H$ -bond MO based on the distance from the  $O$  nucleus to the  $H1s$  electron compared to those of the  $O2p$  electrons. Thus, the MO surface comprises a prolate spheroid at each  $H$  proton that is continuous with the  $2p$  shell at the  $O$  atom. The sum of the energies of the prolate spheroids is matched to that of the  $2p$  shell.

The orbital energy  $E$  for each elliptical cross section of the prolate spheroidal MO is given by the sum of the kinetic  $T$  and potential  $V$  energies.  $E = T + V$  is constant, and the closed orbits are those for which  $T < |V|$ , and the open orbits are those for which  $T \geq |V|$ . It can be shown that the time average of the kinetic energy,  $\langle T \rangle$ , for elliptic motion in an inverse-squared field is  $1/2$  that of the time average of the magnitude of the potential energy,  $\langle |V| \rangle$ .  $\langle T \rangle = 1/2 \langle |V| \rangle$  [11]. In the case of an atomic orbital (AO),  $E = T + V$ , and for all points on the AO,  $|E| = T = 1/2 |V|$ . As shown in the Hydrogen-type Molecular Ions section, each point or coordinate position on the continuous two-dimensional electron MO defines an infinitesimal mass-density element which moves along an orbit comprising an elliptic plane cross section of the spheroidal MO through the foci. The motion is such that eccentric angle,  $\theta$ , changes at a constant rate at each point. That is  $\theta = \omega t$  at time  $t$  where  $\omega$  is a constant, and

$$r(t) = \mathbf{i}a \cos \omega t + \mathbf{j}b \sin \omega t \quad (13.161)$$

Consider the boundary condition that the MO of  $H_2O$  comprises a linear combination of an oxygen AO and two  $H_2$ -type ellipsoidal MOs, one for each  $O-H$ -bond. The charge density of each  $H_2$ -type ellipsoidal MO given by Eqs. (11.44-11.45) and (13.3-13.4) maintains that the surface is an equipotential; however, the potential and kinetic energy of a point on the surface changes as it orbits the central field. The potential energy is a maximum and the kinetic energy is a minimum at the semimajor axis, and the reverse occurs at the semiminor

axis. Since the time average of the kinetic energy,  $\langle T \rangle$ , for elliptic motion in an inverse-squared field is 1/2 that of the time average of the magnitude of the potential energy, by symmetry, the  $\langle T \rangle = 1/2 \langle |V| \rangle$  condition holds for 1/2 of each  $H_2$ -type ellipsoidal MO having the  $H$  focus and ending at the plane defined by the semiminor axes. The  $O$  nucleus  
 5 comprises the other focus of each  $OH$ -MO component of the  $H_2O$  MO. The  $O2p$  AO obeys the energy relationship for all points. Thus, the linear combination of the  $H_2$ -type ellipsoidal MO with the  $O2p$  AO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the  $O2p$  AO in order to match the energy relationships. Thus, the  $H_2O$  MO must comprise two  $O-H$  -bonds with each comprising 75% of a  $H_2$ -type ellipsoidal  
 10 MO (1/2 +25%) and an oxygen AO:

$$[1 O2p_z AO + 0.75 H_2 MO] + [1 O2p_y AO + 0.75 H_2 MO] \rightarrow H_2O MO \quad (13.162)$$

The force balance of the  $H_2O$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.162). The force constant  $k$   
 15 of a  $H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by Eq. (11.65):

$$k = \frac{2e^2}{4\pi\epsilon_o} \quad (13.163)$$

Since the each  $H_2$ -type ellipsoidal MO comprises 75% of the  $O-H$  -bond MO, the electron charge density in Eq. (13.163) is given by  $-0.75e$ . Thus,  $k'$  of the each  $H_2$ -type-ellipsoidal-  
 20 MO component of the  $H_2O$  MO is

$$k' = \frac{(0.75)2e^2}{4\pi\epsilon_o} \quad (13.164)$$

$L$  for the electron equals  $\hbar$ ; thus, the distance from the origin of each  $O-H$  -bond MO to each focus  $c'$  is given by Eqs. (11.79) and (13.164):

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_o}{m_e e^2 1.5a}} = \sqrt{\frac{2aa_0}{3}} \quad (13.165)$$

25 The internuclear distance from Eq. (13.165) is

$$2c' = 2\sqrt{\frac{2aa_0}{3}} \quad (13.166)$$

The length of the semiminor axis of the prolate spheroidal  $O-H$  -bond MO  $b = c$  given by Eq. (11.80) is

$$b = \sqrt{a^2 - c'^2} \quad (13.167)$$

The eccentricity,  $e$ , is

$$5 \quad e = \frac{c'}{a} \quad (13.168)$$

The solution of the semimajor axis  $a$  then allows for the solution of the other axes of the prolate spheroid and eccentricity of the  $O-H$  -bond MO.

The general equation of the ellipsoidal MO having semiprincipal axes  $a, b, c$  given by

$$10 \quad \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \quad (13.169)$$

is also completely determined by the total energy  $E$  given by Eq. (11.18):

$$r = \frac{m \frac{L^2}{m^2} k^{-1}}{1 + \left( 1 + 2Em \frac{L^2}{m^2} k^{-2} \right)^{1/2} \cos \theta} \quad (13.170)$$

The energy of the oxygen  $2p$  shell is the negative of the ionization energy of the oxygen atom given by Eqs. (10.163) and (13.66). Experimentally, the energy is [12]

$$15 \quad E(2p \text{ shell}) = -E(\text{ionization}; O) = -13.6181 \text{ eV} \quad (13.171)$$

Since each of the two prolate spheroidal  $O-H$  -bond MOs comprises a  $H_2$  -type-ellipsoidal MO that transitions to the  $O$  AO, the energy  $E$  in Eq. (13.171) adds to that of the two corresponding  $H_2$  -type ellipsoidal MOs to give the total energy of the  $H_2O$  MO. From the energy equation and the relationship between the axes given by Eqs. (13.165-13.168), the dimensions of the  $H_2O$  MO are solved.

The energy components defined previously for the molecule, Eqs. (11.207-11.212), apply in the case of  $H_2O$ . Since the  $H_2O$  MO comprises two equivalent  $O-H$  -bond MOs, each a linear combination of a  $H_2$  -type-ellipsoidal MO and an  $O2p$  AO, the corresponding energy component of the  $H_2O$  MO is given by the linear superposition of the component energies. Thus, the energy scale factor is given as two times the force factor, the term in parentheses in Eq. (13.164). In addition to the equivalence and linearity principles, this factor also arises from the consideration of the nature of each bond and the linear combination that

forms the  $H_2O$  MO. Each  $O-H$  -bond-energy component is the total for the two equivalent electrons with the exception that the total charge of the two electrons is normalized over the three basis set functions, two  $O-H$  -bond MOs ( $OH$ -type ellipsoidal MOs given in the Energies of  $OH$  section) and one  $O2p$  AO. Thus, the contribution of the  $O-H$  -bond MOs to the  $H_2O$  MO energies are those given for  $H_2(1/p)$  in the Energies of Hydrogen-Type Molecules multiplied by a factor of  $3/2$  as in the case with  $H_3^+$  (Eqs. (13.12), (13.15), 13.18-13.20)). In addition, the two sets of equivalent nuclear-point-charge pairs give rise to a factor of two times the proton-proton repulsion energy given by Eq. (11.208). Thus, the component energies of the  $H_2O$  MO are twice the corresponding energies of the  $OH$  MO given by Eqs. (13.67-13.73). The parameters  $a$ ,  $b$ , and  $c'$  are given by Eqs. (13.165-13.167), respectively.

$$V_e = 2 \left( \frac{3}{4} \right) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \left( \frac{3}{2} \right) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \quad (13.172)$$

$$V_p = 2 \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \quad (13.173)$$

$$T = 2 \left( \frac{3}{4} \right) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \left( \frac{3}{2} \right) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \quad (13.174)$$

$$V_m = 2 \left( \frac{3}{4} \right) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \left( \frac{3}{2} \right) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \quad (13.175)$$

$$E_T = V_e + T + V_m + V_p \quad (13.176)$$

$$E_T = -\frac{e^2}{4\pi\epsilon_0\sqrt{a^2-b^2}} \left[ \left( \frac{3}{2} - \frac{3}{4} \frac{a_0}{a} + \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} - 1 \right] \quad (13.177)$$

$$E_T = -\frac{e^2}{4\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \quad (13.178)$$

Since the each prolate spheroidal  $H_2$ -type MO transitions to the  $O$  AO and the energy of the  $O2p$  shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.171), the total energy  $E_T(H_2O)$  of the  $H_2O$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $O$  AO and the two  $H_2$ -type ellipsoidal MOs that forms the  $H_2O$  MO as given by Eq. (13.162):

$$\begin{aligned}
E_T(H_2O) &= E_T + E(2p \text{ shell}) \\
&= E_T - E(\text{ionization}; O) \\
&= -\frac{e^2}{4\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 13.6181 \text{ eV}
\end{aligned} \tag{13.179}$$

The two hydrogen atoms and the oxygen atom can achieve an energy minimum as a linear combination of two  $H_2$ -type ellipsoidal MOs each having the proton and the oxygen nucleus as the foci. Each  $O-H$ -bond MO comprises the same  $O2p$  shell of constant energy given by Eq. (13.171). Thus, the energy of the  $H_2O$  MO is also given by the sum of that of the two  $H_2$ -type ellipsoidal MOs given by Eq. (11.212) minus the energy of the redundant oxygen atom of the linear combination given by Eq. (13.171):

$$\begin{aligned}
E_T(2H_2 - O) &= -2 \frac{e^2}{8\pi\epsilon_0 a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] - E(2p \text{ shell}) \\
&= 2(-31.63536831 \text{ eV}) - (-13.6181 \text{ eV}) \\
&= -49.652637 \text{ eV}
\end{aligned} \tag{13.180}$$

$E_T(H_2O)$  given by Eq. (13.179) is set equal to two times the energy of the  $H_2$ -type ellipsoidal MO minus the energy of the  $O2p$  shell given by Eq. (13.180):

$$\begin{aligned}
E_T(H_2O) &= -\frac{e^2}{4\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 13.6181 \text{ eV} = -49.652637 \text{ eV} \\
&\tag{13.181}
\end{aligned}$$

From the energy relationship given by Eq. (13.181) and the relationship between the axes given by Eqs. (13.165-13.167), the dimensions of the  $H_2O$  MO can be solved.

Substitution of Eq. (13.165) into Eq. (13.181) gives

$$\frac{e^2}{4\pi\epsilon_0 \sqrt{\frac{2aa_0}{3}}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right] = e36.034537 \tag{13.182}$$

The most convenient way to solve Eq. (13.182) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.2641a_0 = 6.68933 \times 10^{-11} \text{ m} \tag{13.183}$$

Substitution of Eq. (13.183) into Eq. (13.165) gives

$$c' = 0.918005a_0 = 4.85787 \times 10^{-11} \text{ m} \tag{13.184}$$

The internuclear distance given by multiplying Eq. (13.184) by two is

$$2c' = 1.83601a_0 = 9.71574 \times 10^{-11} \text{ m} \quad (13.185)$$

The experimental bond distance is [23]

$$2c' = 9.70 \pm .005 \times 10^{-11} \text{ m} \quad (13.186)$$

Substitution of Eqs. (13.177-13.176) into Eq. (13.167) gives

$$5 \quad b = c = 0.869031a_0 = 4.59871 \times 10^{-11} \text{ m} \quad (13.187)$$

Substitution of Eqs. (13.177-13.176) into Eq. (13.168) gives

$$e = 0.726212 \quad (13.188)$$

The nucleus of the  $H$  atom and the nucleus of the  $O$  atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of each  $H_2$ -type  
 10 ellipsoidal MO and the  $O2p_y$  AO or  $O2p_z$  AO can be determined from the polar equation of the ellipse (Eq. (11.10)):

$$r = r_0 \frac{1+e}{1+e \cos \theta'} \quad (13.189)$$

The radius of the  $O2p$  shell given by Eq. (10.162) is  $r_s = a_0$ , and the polar radial coordinate of the ellipse and the radius of the  $O2p$  shell are equal at the point of intersection. Thus, Eq.  
 15 (13.189) becomes

$$a_0 = (a - c') \frac{1 + \frac{c'}{a}}{1 + \frac{c'}{a} \cos \theta'} \quad (13.190)$$

such that the polar angle  $\theta'$  is given by

$$\theta' = \cos^{-1} \left( \frac{a}{c'} \left( (a - c') \frac{1 + \frac{c'}{a}}{a_0} - 1 \right) \right) \quad (13.191)$$

Substitution of Eqs. (13.177-13.176) into Eq. (13.191) gives

$$20 \quad \theta' = 123.66^\circ \quad (13.192)$$

Then, the angle  $\theta_{O2pAO}$  the radial vector of the  $O2p$  AO makes with the internuclear axis is

$$\theta_{O2pAO} = 180^\circ - 123.66^\circ = 56.33^\circ \quad (13.193)$$

as shown in Figure 7. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{H_2MO}$   
 25 between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the  $O$  radial vector obeys the following relationship:

$$a_0 \sin \theta_{O2pAO} = b \sin \theta_{H_2MO} \quad (13.194)$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{a_0 \sin \theta_{O2pAO}}{b} = \sin^{-1} \frac{a_0 \sin 56.33^\circ}{b} \quad (13.195)$$

with the use of Eq. (13.193). Substitution of Eq. (13.188) into Eq. (13.195) gives

$$5 \quad \theta_{H_2MO} = 73.28^\circ \quad (13.196)$$

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a \cos \theta_{H_2MO} \quad (13.197)$$

Substitution of Eqs. (13.183) and (13.196) into Eq. (13.197) gives

$$10 \quad d_{H_2MO} = 0.3637a_0 = 1.9244 \times 10^{-11} \text{ m} \quad (13.198)$$

The distance  $d_{O2pAO}$  along the internuclear axis from the origin of the  $O$  atom to the point of intersection of the orbitals is given by

$$d_{O2pAO} = c' - d_{H_2MO} \quad (13.199)$$

Substitution of Eqs. (13.184) and (13.198) into Eq. (13.199) gives

$$15 \quad d_{O2pAO} = 0.5543a_0 = 2.93343 \times 10^{-11} \text{ m} \quad (13.200)$$

In addition to the intersection of the  $H_2$ -type MO with the  $O2p$  shell, two adjoining ellipsoidal  $H_2$ -type MOs intersect at points of equipotential. The angle and distance parameters are given by Eqs. (13.595-13.600) for the limiting methane case wherein four adjoining intersecting  $H_2$ -type MOs have the possibility of forming a self-contained two-  
 20 dimension equipotential surface of charge and current. Charge continuity can be obeyed for the  $H_2O$  MO if the current is continuous between the adjoining  $H_2$ -type MOs. However, in the limiting case of methane, the existence of a separate linear combination of the  $H_2$ -type MOs comprising four-spin paired electrons, not connected to the bonding carbon heteroatom requires that the electron be divisible. It is possible for an electron to form time-dependent  
 25 singular points or nodes having no charge as shown by Eqs. (1.65a-1.65b), and two-dimensional charge distributions having Laplacian potentials and one-dimensional regions of zero charge are possible for macroscopic charge densities and currents as given in Haus and Melcher [24]. However, it is not possible for single electrons to have two dimensional discontinuities in charge based on internal forces and first principles discussed in Appendix



IV. Thus, at the points of intersection of the  $H_2$ -type MOs of methane, symmetry, electron indivisibility, current continuity, and conservation of energy and angular momentum require that the current between the points of mutual contact and the carbon atom be projected onto and flow along the radial vector to the surface of the  $C2sp^3$  shell. This current designed the  
 5 bisector current (BC) meets the  $C2sp^3$  surface and does not travel to distances shorter than its radius. The methane result must also apply in the case of other bonds including that of the water molecule. Here, the  $H_2$ -type MOs intersect and the ellipsoidal current is projected onto the radial vector to the  $O2p$  shell and does not travel to distances shorter than its radius as in the case of a single  $O-H$  bond.

10 As shown in Eq. (13.162), in addition to the  $p$ -orbital charge-density modulation, the uniform charge-density in the  $p_z$  and  $p_y$  orbitals is increased by a factor of 0.25 and the  $H$  atoms are each decreased by a factor of 0.25. Using the orbital composition of  $H_2O$  (Eq. (13.162)), the radii of  $O1s = 0.12739a_0$  (Eq. (10.51)),  $O2s = 0.59020a_0$  (Eq. (10.62)), and  $O2p = a_0$  (Eq. (10.162)) shells, and the parameters of the  $H_2O$  MO given by Eqs. (13.3-  
 15 13.4), (13.183-13.185), (13.187-13.188), and (13.192-13.200), the charge-density of the  $H_2O$  MO comprising the linear combination of two  $O-H$ -bond MOs ( $OH$ -type ellipsoidal MOs given in the Energies of  $OH$  section) according to Eq. (13.162) is shown in Figure 9. Each  $O-H$ -bond MO comprises a  $H_2$ -type ellipsoidal MO and an  $O2p$  AO having the dimensional diagram shown in Figure 8.

20

## ENERGIES OF $H_2O$

The energies of  $H_2O$  given by the substitution of the semiprincipal axes (Eqs. (13.183-13.185) and (13.187)) into the energy equations (Eqs. (13.172-13.180)) are

$$V_e = \left(\frac{3}{2}\right) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -81.8715 \text{ eV} \quad (13.201)$$

$$25 \quad V_p = 2 \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 29.6421 \text{ eV} \quad (13.202)$$

$$T = \left(\frac{3}{2}\right) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 32.3833 \text{ eV} \quad (13.203)$$

$$V_m = \left(\frac{3}{2}\right) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -16.1917 \text{ eV} \quad (13.204)$$

$$E_T(H_2O) = -\frac{e^2}{4\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 13.6181 \text{ eV} = -49.6558 \text{ eV} \quad (13.205)$$

where  $E_T(H_2O)$  is given by Eq. (13.179) which is reiteratively matched to Eq. (13.180) within five-significant-figure round-off error.

5

## VIBRATION OF $H_2O$

The vibrational energy levels of  $H_2O$  may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as  
10 given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERM OF $H_2O$

The radiation reaction force in the case of the vibration of  $H_2O$  in the transition state  
15 corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) and Eqs. (13.22) and (13.144) that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. As in the case of  $H_3^+$ , the water molecule is a linear combination of three orbitals. The water MO comprises two  $H_2$ -type ellipsoidal MOs and the  $O$  AO. Thus, the force factor of water in the determination  
20 of the Doppler frequency is equivalent to that of the  $H_3^+$  ion given in Eqs. (13.18-13.20) and given by Eq. (13.164). From Eqs. (11.231-11.232) and (13.18-13.20), the central force terms between the electron density and the nuclei of each  $O-H$ -bond MO with the radius of the orbit at the oxygen atom fixed at

$$r_8 = a_0 \quad (13.206)$$

25 according to Eq. (10.162) with the oscillation along the semiminor axis are

$$f(b) = -\left(\frac{3}{2}\right) \frac{e^2}{4\pi\epsilon_0 b^2} \quad (13.207)$$

and

$$f'(b) = \left(\frac{3}{2}\right) \frac{2e^2}{4\pi\epsilon_0 b^3} \quad (13.208)$$

Thus, using Eqs. (11.136) and (13.207-13.208), the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\left(\frac{3}{2}\right) \frac{e^2}{4\pi\epsilon_0 b^3}}{m_e}} = 6.24996 \times 10^{16} \text{ rad/s} \quad (13.209)$$

The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$5 \quad \bar{E}_K = \hbar\omega = \hbar 6.24996 \times 10^{16} \text{ rad/s} = 41.138334 \text{ eV} \quad (13.210)$$

The three basis elements of water,  $H$ ,  $H$ , and  $O$ , all have the same Coulombic energy as given by Eqs. (1.243) and (10.163), respectively, such that the Doppler energy involves the total energy of the  $H_2O$  MO. Thus, in Eq. (11.181), substitution of the total energy of  $H_2O$ ,  $E_T(H_2O)$ , (Eqs. (13.179-13.180) and Eq. (13.181)) for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  
 10  $M$ , and the kinetic energy given by Eq. (13.210) for  $\bar{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -49.652637 \text{ eV} \sqrt{\frac{2e(41.138334 \text{ eV})}{m_e c^2}} = -0.630041 \text{ eV} \quad (13.211)$$

The total energy of  $H_2O$  is decreased by  $\bar{E}_D$ .

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the  
 15 transition state at their corresponding frequency. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [4]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons,  $\bar{E}_{Kvib}$ , is 1/2 of the vibrational energy of  $H_2O$ . The decrease in the energy of  $H_2O$  due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and  
 20 nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  and  $\bar{E}_{Kvib}$ . Using Eq. (13.211) and the experimental  $H^{16}OH$  vibrational energy of  $E_{vib} = 3755.93 \text{ cm}^{-1} = 0.465680 \text{ eV}$  [25] gives

$$\bar{E}'_{osc} = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.212)$$

$$\bar{E}'_{osc} = -0.630041 \text{ eV} + \frac{1}{2} (0.465680 \text{ eV}) = -0.397201 \text{ eV} \quad (13.213)$$

per bond. As in the case for  $H_3^+(1/p)$  shown in the Doppler Energy Term of  $H_3^+$ -type Molecular Ions section, the reentrant orbit for the binding of a hydrogen atom to a hydroxyl radical causes the bonds to oscillate by increasing and decreasing in length along the two  $O-H$  bonds at a relative phase angle of  $180^\circ$ . Since the vibration and reentrant oscillation is along two bonds for the asymmetrical stretch ( $\nu_3$ ),  $\bar{E}_{osc}$  for  $H^{16}OH$ ,  $\bar{E}_{osc}(H^{16}OH)$ , is:

$$\begin{aligned}\bar{E}_{osc}(H^{16}OH) &= 2 \left( \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \\ &= 2 \left( -0.630041 \text{ eV} + \frac{1}{2} (0.465680 \text{ eV}) \right) \\ &= -0.794402 \text{ eV}\end{aligned}\tag{13.214}$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies,  $\bar{E}_K$ , are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies per bond. Using Eq. (13.211), Eqs. (13.212-13.214), and the experimental  $D^{16}OD$  vibrational energy of  $E_{vib} = 2787.92 \text{ cm}^{-1} = 0.345661 \text{ eV}$  [25], the corresponding  $\bar{E}_{osc}(D^{16}OD)$  is

$$\begin{aligned}\bar{E}_{osc}(D^{16}OD) &= 2 \left( -0.630041 \text{ eV} + \frac{1}{2} (0.345661 \text{ eV}) \right) \\ &= -0.914421 \text{ eV}\end{aligned}\tag{13.215}$$

## 15 TOTAL AND BOND ENERGIES OF $H^{16}OH$ AND $D^{16}OD$

$E_{T+osc}(H_2^{16}O)$ , the total energy of the  $H^{16}OH$  including the Doppler term, is given by the sum of  $E_T(H_2O)$  (Eq. (13.181)) and  $\bar{E}_{osc}(H^{16}OH)$  given Eqs. (13.207-13.214):

$$\begin{aligned}E_{T+osc}(H_2^{16}O) &= V_e + T + V_m + V_p + E(O2p) + \bar{E}_{osc}(H^{16}OH) \\ &= E_T(H_2O) + \bar{E}_{osc}(H^{16}OH)\end{aligned}\tag{13.216}$$

$$E_{T+osc}(H_2^{16}O) = \left\{ \left( \frac{-e^2}{4\pi\epsilon_0 c'} \left( \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right) - 13.6181 \text{ eV} \right) \left( 1 + 2 \sqrt{\frac{2\hbar \sqrt{\frac{3}{2} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2}} \right) + 2 \left( \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \right\}$$

$$= -49.652637 \text{ eV} - 2 \left( 0.630041 \text{ eV} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \quad (13.217)$$

From Eqs. (13.214) and (13.216-13.217), the total energy of  $H^{16}OH$  is

$$\begin{aligned} E_{T+osc}(H_2^{16}O) &= -49.652637 \text{ eV} + \bar{E}_{osc}(H^{16}OH) \\ &= -49.652637 \text{ eV} - 2 \left( 0.630041 \text{ eV} - \frac{1}{2} (0.465680 \text{ eV}) \right) \\ &= -50.447039 \text{ eV} \end{aligned} \quad (13.218)$$

5 where the experimental vibrational energy was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.  $E_{T+osc}(D_2^{16}O)$ , the total energy of  $D^{16}OD$  including the Doppler term is given by the sum of  $E_T(D_2O) = E_T(H_2O)$  (Eq. (13.181)) and  $\bar{E}_{osc}(D^{16}OD)$  given by Eq. (13.215):

$$\begin{aligned} E_{T+osc}(D_2^{16}O) &= -49.652637 \text{ eV} + \bar{E}_{osc}(D^{16}OD) \\ &= -49.652637 \text{ eV} - 2 \left( 0.630041 \text{ eV} - \frac{1}{2} (0.345661 \text{ eV}) \right) \\ &= -50.567058 \text{ eV} \end{aligned} \quad (13.219)$$

where the experimental vibrational energy was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term. As in the case of the

10 hydroxyl radical, the dissociation of the bond of the water molecule forms a free hydrogen atom and a hydroxyl radical, with one unpaired electron each. The lowering of the energy of the reactants due to the magnetic dipoles decreases the bond energy. Thus, the total energy of oxygen is reduced by the energy in the field of the two magnetic dipoles given by Eq. (13.152). The corresponding bond dissociation energy,  $E_D$ , is given by the sum of the total

energies of the corresponding hydroxyl radical and hydrogen atom minus the total energy of water,  $E_{T+osc}(H^{16}OH)$ , and  $E(magnetic)$ .

Thus,  $E_D$  of  $H^{16}OH$  is given by:

$$E_D(H^{16}OH) = E(H) + E(^{16}OH) - E_{T+osc}(H^{16}OH) - E(magnetic) \quad (13.220)$$

5 where  $E_T(^{16}OH)$  is given by the of the sum of the experimental energies of  $^{16}O$  (Eq. (13.171)),  $H$  (Eq. (13.154)), and the negative of the bond energy of  $^{16}OH$  (Eq. (13.157)):

$$E(^{16}OH) = -13.59844 \text{ eV} - 13.6181 \text{ eV} - 4.41174 \text{ eV} = -31.62828 \text{ eV} \quad (13.221)$$

From Eqs. (13.154), (13.218), and (13.220-13.221),  $E_D(H^{16}OH)$  is

$$\begin{aligned} E_D(H^{16}OH) &= E(H) + E(^{16}OH) - (E(magnetic) + E_{T+osc}(H^{16}OH)) \\ &= -13.59844 \text{ eV} - 31.62828 \text{ eV} - (0.114411 \text{ eV} - 50.447039 \text{ eV}) \\ &= 5.1059 \text{ eV} \end{aligned}$$

10 (13.222)

The experimental  $H^{16}OH$  bond dissociation energy is [26]

$$E_D(H^{16}OH) = 5.0991 \text{ eV} \quad (13.223)$$

Similarly,  $E_D$  of  $D^{16}OD$  is given by:

$$E_D(D^{16}OH) = E(D) + E(^{16}OD) - (E(magnetic) + E_{T+osc}(D^{16}OD)) \quad (13.224)$$

15 where  $E_T(^{16}OD)$  is given by the of the sum of the experimental energies of  $^{16}O$  (Eq. (13.171)),  $D$  (Eq. (13.155)), and the negative of the bond energy of  $^{16}OD$  (Eq. (13.159)):

$$E(^{16}OD) = -13.603 \text{ eV} - 13.6181 \text{ eV} - 4.454 \text{ eV} = -31.6721 \text{ eV} \quad (13.225)$$

From Eqs. (13.155), (13.220), and (13.224-13.225),  $E_D(D^{16}OD)$  is

$$\begin{aligned} E_D(D^{16}OD) &= -13.603 \text{ eV} - 31.6721 \text{ eV} - (0.114411 \text{ eV} - 50.567058 \text{ eV}) \\ &= 5.178 \text{ eV} \end{aligned} \quad (13.226)$$

20 The experimental  $D^{16}OD$  bond dissociation energy is [27]

$$E_D(D^{16}OD) = 5.191 \text{ eV} \quad (13.227)$$

## BOND ANGLE OF $H_2O$

The  $H_2O$  MO comprises a linear combination of two  $O-H$ -bond MOs. Each  $O-H$ -bond  
25 MO comprises the superposition of a  $H_2$ -type ellipsoidal MO and the  $O2p_z$  AO or the

$O2p_y$  AO with a relative charge-density of 0.75 to 1.25; otherwise, the  $O2p$  orbitals are the same as those of the oxygen atom. A bond is also possible between the two H atoms of the  $O-H$  bonds. Such  $H-H$  bonding would decrease the  $O-H$  -bond strength since electron density would be shifted from the  $O-H$  bonds to the  $H-H$  bond. Thus, the bond angle  
 5 between the two  $O-H$  bonds is determined by the condition that the total energy of the  $H_2$  -type ellipsoidal MO between the terminal H atoms of the  $O-H$  bonds is zero. Since the two  $H_2$  -type ellipsoidal MOs comprise 75% of the H electron density of  $H_2$ ; the energies and the total energy  $E_T$  of the  $H-H$  bond is given by Eqs. (13.67-13.73). From Eq. (11.79), the distance from the origin to each focus of the  $H-H$  ellipsoidal MO is

$$10 \quad c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \quad (13.228)$$

The internuclear distance from Eq. (13.228) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \quad (13.229)$$

The length of the semiminor axis of the prolate spheroidal  $H-H$  MO  $b = c$  is given by Eq. (13.167). Substitution of Eq. (13.228) into Eq. (13.73) gives

$$15 \quad E_T = -\frac{e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2}}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right] \quad (13.230)$$

The radiation reaction force in the case of the vibration of  $H-H$  in the transition state corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. The total energy  $E_T$  that includes the radiation reaction of the  $H-H$  MO is given by the sum of  $E_T$  (Eq. (13.73)) and  $\bar{E}_{osc}(H_2)$  given Eqs.  
 20 (11.213-11.220), (11.231-11.236), and (11.239-11.240). Thus, the total energy  $E_T(H-H)$  of the  $H-H$  MO including the Doppler term is

$$E_T = V_e + T + V_m + V_p + \bar{E}_{osc}(H-H) \quad (13.231)$$

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$$\begin{aligned}
E_T &= \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} \right] + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \\
&= \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} \right] \\
&\quad + \frac{1}{2} \hbar \sqrt{\frac{\frac{0.75e^2}{8\pi\epsilon_0 a^3} - \frac{e^2}{8\pi\epsilon_0 (a+c')^3}}{0.5m_p}}
\end{aligned} \tag{13.232}$$

To match the boundary condition that the total energy of the  $H-H$  ellipsoidal MO is zero,  $E_T(H-H)$  given by Eq. (13.232) is set equal to zero:

$$0 = \left[ \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} \right] \right. \\
\left. + \frac{1}{2} \hbar \sqrt{\frac{\frac{0.75e^2}{8\pi\epsilon_0 a^3} - \frac{e^2}{8\pi\epsilon_0 (a+c')^3}}{0.5m_p}} \right] \tag{13.233}$$

5 From the energy relationship given by Eq. (13.233) and the relationship between the axes given by Eqs. (13.165-13.167), the dimensions of the  $H-H$  MO can be solved.

The most convenient way to solve Eq. (13.233) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 4.300a_0 = 2.275 \times 10^{-10} \text{ m} \tag{13.234}$$

10 Substitution of Eq. (13.234) into Eq. (13.228) gives

$$c' = 1.466a_0 = 7.759 \times 10^{-11} \text{ m} \tag{13.235}$$

The internuclear distance given by multiplying Eq. (13.235) by two is

$$2c' = 2.933a_0 = 1.552 \times 10^{-10} \text{ m} \tag{13.236}$$

Substitution of Eqs. (13.234-13.235) into Eq. (13.167) gives

$$15 \quad b = c = 4.042a_0 = 2.139 \times 10^{-10} \text{ m} \tag{13.237}$$

Substitution of Eqs. (13.234-13.235) into Eq. (13.168) gives



$$e = 0.341 \quad (13.238)$$

Using, distance between the two  $H$  atoms when the total energy of the corresponding MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$A^2 + B^2 - 2AB\cosine\theta = C^2 \quad (13.239)$$

- 5 With  $A = B = 2c'_{O-H}$ , the internuclear distance of each  $O-H$  bond given by Eq. (13.185), and  $C = 2c'_{H-H}$ , the internuclear distance of the two  $H$  atoms, the bond angle between the  $O-H$  bonds is given by

$$(2c'_{O-H})^2 + (2c'_{O-H})^2 - 2(2c'_{O-H})^2 \cos\theta = (2c'_{H-H})^2 \quad (13.240)$$

$$\theta = \cos^{-1} \left( \frac{2(2c'_{O-H})^2 - (2c'_{H-H})^2}{2(2c'_{O-H})^2} \right) \quad (13.241)$$

- 10 Substitution of Eqs. (13.185) and (13.236) into Eq. (13.241) gives

$$\begin{aligned} \theta &= \cos^{-1} \left( \frac{2(1.836)^2 - (2.933)^2}{2(1.836)^2} \right) \\ &= \cos^{-1}(-0.2756) \\ &= 105.998^\circ \end{aligned} \quad (13.242)$$

The experimental internuclear distance of the two  $H$  atoms,  $2c'_{H-H}$ , is [23]

$$2c'_{H-H} = 1.55 \pm 0.01 \times 10^{-10} \text{ m} \quad (13.243)$$

which matches Eq. (13.236) very well. The experimental angle between the  $O-H$  bonds is

15 [23]

$$\theta = 106^\circ \quad (13.244)$$

which matches the predicted angle given by Eq. (13.242).

- The results of the determination of bond parameters of  $H_2O$  and  $D_2O$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## **HYDROGEN NITRIDE ( $NH$ )**

- The ammonia molecule can be solved by first considering the solution of the hydrogen and dihydrogen nitride radicals. The former is formed by the reaction of a hydrogen atom and a nitrogen atom:



The hydrogen nitride radicals,  $NH$  and  $NH_2$ , and ammonia,  $NH_3$ , can be solved using the same principles as those used to solve  $OH$  and  $H_2O$ .

### FORCE BALANCE OF $NH$

- 5  $NH$  comprises two spin-paired electrons in a chemical bond between the nitrogen atom and the hydrogen atom such that two electrons on  $N$  remain unpaired. The  $NH$  radical molecular orbital (MO) is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal  $H_2$  MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus,
- 10 the  $H$ -atom electron forms a  $H_2$ -type ellipsoidal MO with one of the  $N$ -atom electrons. The  $N$  electron configuration given in the Seven-Electron Atoms section is  $1s^2 2s^2 2p^3$ , and the orbital arrangement is

$$\begin{array}{ccc} & \text{2p state} & \\ \uparrow & \uparrow & \uparrow \\ \hline 1 & 0 & -1 \end{array} \quad (13.246)$$

- corresponding to the ground state  $^4S_{3/2}^0$ . The  $N2p_x$  electron combines with the  $H1s$
- 15 electron to form a molecular orbital. The proton of the  $H$  atom is along the internuclear axis. Due to symmetry, the other  $N$  electrons are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix IV.) Thus, the energies in the  $NH$  MO involve only the  $N2p_x$  and  $H1s$  electrons and the change in the magnetic energy of the  $N2p_x$  electron with the other  $N$  electrons (Eq. (13.305)) with the formation of the  $NH$  MO. The forces are
- 20 determined by these energies.

As in the case of  $H_2$ , the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $N$  atom for distances shorter than the radius of the  $2p$  shell. Thus, the MO surface comprises a prolate spheroid at the  $H$  proton that is continuous with the  $2p$  shell at the  $N$  atom whose nucleus serves as the other focus. The

25 energy of the prolate spheroid is matched to that of the  $N2p$  shell. As in the case with  $OH$ , the linear combination of the  $H_2$ -type ellipsoidal MO with the  $N2p$  AO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the  $N2p$  atomic orbital (AO) in order to match potential, kinetic, and orbital energy relationships. Thus, the  $NH$  MO must comprise 75% of a  $H_2$ -type ellipsoidal MO and a nitrogen AO:



The force balance of the  $NH$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.247) and the energy matching condition between the hydrogen and nitrogen components of the MO.

Similar to the  $OH$  case given by Eq. (13.59), the  $H_2$ -type ellipsoidal MO comprises 75% of the  $NH$  MO; so, the electron charge density in Eq. (11.65) is given by  $-0.75e$ . Based on the condition that the electron MO is an equipotential energy surface, Eq. (11.79) gives the ellipsoidal parameter  $c'$  in terms of the central force of the foci, the electron angular momentum, and the ellipsoidal parameter  $a$ . To meet the equipotential condition of the union of the  $H_2$ -type-ellipsoidal-MO and the  $N$  AO, the force constant used to determine the ellipsoidal parameter  $c'$  is normalized by the ratio of the ionization energy of  $N$  14.53414 eV [6] and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). This normalizes the force to match that of the Coulombic force alone to meet the force matching condition of the  $NH$  MO under the influence of the proton and the  $N$  nucleus. Thus,  $k'$  of Eq. (11.79) to determine  $c'$  is

$$k' = \frac{(0.75)2e^2}{4\pi\epsilon_0 \frac{14.53414}{13.605804}} = (0.936127) \frac{(0.75)2e^2}{4\pi\epsilon_0} \quad (13.248)$$

$L$  for the electron equals  $\hbar$ ; thus, the distance from the origin of the  $NH$  MO to each focus  $c'$  is given by Eqs. (11.79) and (13.248):

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 1.5a (0.936127)}} = \sqrt{\frac{2aa_0}{3(0.936127)}} = \sqrt{0.712154aa_0} \quad (13.249)$$

The internuclear distance from Eq. (13.249) is

$$2c' = 2\sqrt{0.712154aa_0} \quad (13.250)$$

The length of the semiminor axis of the prolate spheroidal  $NH$  MO  $b = c$  is given by Eqs. (11.80) and (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). Then, the solution of the semimajor axis  $a$  allows for the solution of the other axes of the prolate spheroidal and eccentricity of the  $NH$  MO.

The energy of the nitrogen  $2p$  shell is the negative of the ionization energy of the nitrogen atom given by Eq. (10.143). Experimentally, the energy is [6]

$$E(2p \text{ shell}) = -E(\text{ionization}; N) = -14.53414 \text{ eV} \quad (13.251)$$

Since the prolate spheroidal MO transitions to the  $N$  AO, the energy  $E$  in Eq. (13.251) adds to that of the  $H_2$ -type ellipsoidal MO to give the total energy of the  $NH$  MO. From the energy equation and the relationship between the axes given by Eqs. (13.249-13.250) and 5 (13.62-13.63), the dimensions of the  $NH$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  are the same as those of  $OH$  given by Eqs. (13.67-13.73). Similarly to  $OH$ , the total energy  $E_T(NH)$  of the  $NH$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $N$  AO and the  $H_2$ -type ellipsoidal MO that forms the  $NH$  MO as given 10 by Eq. (13.247):

$$\begin{aligned} E_T(NH) &= E_T + E(2p \text{ shell}) \\ &= E_T - E(\text{ionization}; N) \\ &= -\frac{e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV} \end{aligned} \quad (13.252)$$

To match the boundary condition that the total energy of the entire the  $H_2$ -type ellipsoidal MO is given by Eqs. (11.212) and (13.75),  $E_T(NH)$  given by Eq. (13.252) is set equal to Eq. (13.75):

$$15 \quad E_T(NH) = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV} = -31.63536831 \text{ eV} \quad (13.253)$$

From the energy relationship given by Eq. (13.252) and the relationship between the axes given by Eqs. (13.249-13.250) and (13.62-13.63), the dimensions of the  $NH$  MO can be solved.

20 Substitution of Eq. (13.249) into Eq. (13.253) gives

$$\frac{e^2}{8\pi\epsilon_0 \sqrt{0.712154aa_0}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{0.712154aa_0}}{a - \sqrt{0.712154aa_0}} - 1 \right] = e17.10123 \quad (13.254)$$

The most convenient way to solve Eq. (13.254) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.36275a_0 = 7.21136 \times 10^{-11} \text{ m} \quad (13.255)$$

25 Substitution of Eq. (13.255) into Eq. (13.249) gives

$$c' = 0.98513a_0 = 5.21310 \times 10^{-11} \text{ m} \quad (13.256)$$

The internuclear distance given by multiplying Eq. (13.256) by two is

$$2c' = 1.97027a_0 = 1.04262 \times 10^{-10} \text{ m} \quad (13.257)$$

The experimental bond distance is [28]

$$2c' = 1.0362 \times 10^{-10} \text{ m} \quad (13.258)$$

5 Substitution of Eqs. (13.255-13.256) into Eq. (13.62) gives

$$b = c = 0.94159a_0 = 4.98270 \times 10^{-11} \text{ m} \quad (13.259)$$

Substitution of Eqs. (13.255-13.256) into Eq. (13.63) gives

$$e = 0.72290 \quad (13.260)$$

The nucleus of the  $H$  atom and the nucleus of the  $N$  atom comprise the foci of the  $H_2$ -type  
10 ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $N2p_x$  AO are given by Eqs. (13.84-13.95). The polar intersection angle  $\theta'$  is given by

$$\theta' = \cos^{-1} \left( \frac{a}{c'} \left( (a - c') \frac{1 + \frac{c'}{a}}{r_n} - 1 \right) \right) \quad (13.261)$$

where  $r_n = r_7 = 0.93084a_0$  is the radius of the  $N$  atom. Substitution of Eqs. (13.255-13.256)

15 into Eq. (13.86) gives

$$\theta' = 114.61^\circ \quad (13.262)$$

Then, the angle  $\theta_{N2p_xAO}$  the radial vector of the  $N2p_x$  AO makes with the internuclear axis is

$$\theta_{N2p_xAO} = 180^\circ - 114.61^\circ = 65.39^\circ \quad (13.263)$$

as shown in Figure 10.

20 The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $N$  radial vector obeys the following relationship:

$$r_7 \sin \theta_{N2p_xAO} = 0.93084a_0 \sin \theta_{N2p_xAO} = b \sin \theta_{H_2MO} \quad (13.264)$$

25 such that

$$\theta_{H_2MO} = \sin^{-1} \frac{0.93084a_0 \sin \theta_{N2p_xAO}}{b} = \sin^{-1} \frac{0.93084a_0 \sin 65.39^\circ}{b} \quad (13.265)$$

with the use of Eq. (13.263). Substitution of Eq. (13.259) into Eq. (13.265) gives

$$\theta_{H_2MO} = 64.00^\circ \quad (13.266)$$

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a \cos \theta_{H_2MO} \quad (13.267)$$

5 Substitution of Eqs. (13.255) and (13.266) into Eq. (13.267) gives

$$d_{H_2MO} = 0.59747a_0 = 3.16166 \times 10^{-11} \text{ m} \quad (13.268)$$

The distance  $d_{N2pAO}$  along the internuclear axis from the origin of the  $N$  atom to the point of intersection of the orbitals is given by

$$d_{N2pAO} = c' - d_{H_2MO} \quad (13.269)$$

10 Substitution of Eqs. (13.79) and (13.93) into Eq. (13.94) gives

$$d_{N2pAO} = 0.38767a_0 = 2.05144 \times 10^{-11} \text{ m} \quad (13.270)$$

As shown in Eq. (13.247), in addition to the  $p$ -orbital charge-density modulation, the uniform charge-density in the  $p_x$  orbital is increased by a factor of 0.25 and the  $H$ -atom density is decreased by a factor of 0.25. The internuclear axis of the  $N-H$  bond is  
 15 perpendicular to the bonding  $p_x$  orbital. Using the orbital composition of  $NH$  (Eq. (13.27)), the radii of  $N1s = 0.14605a_0$  (Eq. (10.51)),  $N2s = 0.69385a_0$  (Eq. (10.62)), and  $N2p = 0.93084a_0$  (Eq. (10.142)) shells, and the parameters of the  $NH$  MO given by Eqs. (13.3-13.4) and (13.255-13.270), the dimensional diagram and charge-density of the  $NH$  MO comprising the linear combination of the  $H_2$ -type ellipsoidal MO and the  $N$  AO  
 20 according to Eq. (13.247) are shown in Figures 10 and 11, respectively.

## ENERGIES OF $NH$

The energies of  $NH$  given by the substitution of the semiprincipal axes (Eqs. (13.255-13.256) and (13.259)) into the energy equations (Eqs. (13.67-13.73)) are

$$25 \quad V_e = \left( \frac{3}{4} \right) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -37.85748 \text{ eV} \quad (13.271)$$

$$V_p = \frac{e^2}{8\pi\epsilon_0\sqrt{a^2 - b^2}} = 13.81113 \text{ eV} \quad (13.272)$$

$$T = \left( \frac{3}{4} \right) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 13.89011 \text{ eV} \quad (13.273)$$

$$V_m = \left(\frac{3}{4}\right) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -6.94505 \text{ eV} \quad (13.274)$$

$$E_T(NH) = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV} = -31.63544 \text{ eV} \quad (13.275)$$

where  $E_T(NH)$  is given by Eq. (13.253) which is reiteratively matched to Eq. (13.75) within 5 five-significant-figure round-off error.

### VIBRATION AND ROTATION OF $NH$

The vibrational energy of  $NH$  may be solved in the same manner as that of  $OH$ . From Eqs. (13.102-13.106) with the substitution of the  $NH$  parameters, the angular frequency of the oscillation is

$$\begin{aligned} \omega &= \sqrt{\frac{\frac{0.75e^2}{8\pi\epsilon_0 b^3} - \frac{e^2}{8\pi\epsilon_0 (2c')^3}}{\mu}} \\ &= \sqrt{\frac{\frac{0.75e^2}{8\pi\epsilon_0 (0.94159a_0)^3} - \frac{e^2}{8\pi\epsilon_0 (1.97027a_0)^3}}{\frac{14}{15}m_p}} \\ &= 6.18700 \times 10^{14} \text{ rad/s} \end{aligned} \quad (13.276)$$

where  $b$  is given by Eq. (13.259),  $2c'$  is given by Eq. (13.257), and the reduced mass of  $^{14}NH$  is given by:

$$\mu_{^{14}NH} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1)(14)}{1+14} m_p \quad (13.277)$$

where  $m_p$  is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency,  $\omega(0)$ , for  $^{14}NH$  given by Eqs. (11.136), (11.148), and (13.276) is

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{597.59 \text{ Nm}^{-1}}{\mu}} = 6.18700 \times 10^{14} \text{ radians/s} \quad (13.278)$$

where the reduced nuclear mass of  $^{14}NH$  is given by Eq.(13.277) and the spring constant,  $k(0)$ , given by Eqs. (11.136) and (13.276) is

$$k(0) = 597.59 \text{ Nm}^{-1} \quad (13.279)$$

The  $^{14}\text{NH}$  transition-state vibrational energy,  $E_{\text{vib}}(0)$ , given by Planck's equation (Eq. (11.127)) is:

$$E_{\text{vib}}(0) = \hbar\omega = \hbar 6.18700 \times 10^{14} \text{ rad/s} = 0.407239 \text{ eV} = 3284.58 \text{ cm}^{-1} \quad (13.280)$$

5  $\omega_e$ , from the experimental curve fit of the vibrational energies of  $^{14}\text{NH}$  is [28]

$$\omega_e = 3282.3 \text{ cm}^{-1} \quad (13.281)$$

Using Eqs. (13.112-13.118) with  $E_{\text{vib}}(0)$  given by Eq. (13.280) and  $D_0$  given by Eq. (13.311), the  $^{14}\text{NH}$   $\nu=1 \rightarrow \nu=0$  vibrational energy,  $E_{\text{vib}}(1)$  is

$$E_{\text{vib}}(1) = 0.38581 \text{ eV} \quad (3111.84 \text{ cm}^{-1}) \quad (13.282)$$

10 The experimental vibrational energy of  $^{14}\text{NH}$  using  $\omega_e$  and  $\omega_e x_e$  [28] according to K&P [15] is

$$E_{\text{vib}}(1) = 0.38752 \text{ eV} \quad (3125.5 \text{ cm}^{-1}) \quad (13.283)$$

Using Eq. (13.113) with  $E_{\text{vib}}(1)$  given by Eq. (13.282) and  $D_0$  given by Eq. (13.311), the anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{14}\text{NH}$  is

$$15 \quad \omega_0 x_0 = 86.37 \text{ cm}^{-1} \quad (13.284)$$

The experimental anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{14}\text{NH}$  [28] is

$$\omega_0 x_0 = 78.4 \text{ cm}^{-1} \quad (13.285)$$

The vibrational energies of successive states are given by Eqs. (13.280), (13.112), and (13.284).

20 Using  $b$  given by Eq. (13.259),  $2c'$  given by Eq. (13.257),  $D_0$  given by Eq. (13.314), and the reduced nuclear mass of  $^{14}\text{ND}$  given by

$$\mu_{^{14}\text{ND}} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(2)(14)}{2 + 14} m_p \quad (13.286)$$

where  $m_p$  is the proton mass, the corresponding parameters for deuterium nitride  $^{14}\text{ND}$  (Eqs. (13.102-13.121)) are

$$25 \quad \omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{597.59 \text{ Nm}^{-1}}{\mu}} = 4.51835 \times 10^{14} \text{ radians/s} \quad (13.287)$$

$$k(0) = 579.59 \text{ Nm}^{-1} \quad (13.288)$$



$$E_{vib}(0) = \hbar\omega = \hbar 4.51835 \times 10^{14} \text{ rad/s} = 0.29741 \text{ eV} = 2398.72 \text{ cm}^{-1} \quad (13.289)$$

$$E_{vib}(1) = 0.28710 \text{ eV} \quad (2305.35 \text{ cm}^{-1}) \quad (13.290)$$

$$\omega_0 x_0 = 47.40 \text{ cm}^{-1} \quad (13.291)$$

$\omega_e$ , from the experimental curve fit of the vibrational energies of  $^{14}\text{ND}$  is [28]

$$5 \quad \omega_e = 2398 \text{ cm}^{-1} \quad (13.292)$$

The experimental vibrational energy of  $^{14}\text{ND}$  using  $\omega_e$  and  $\omega_e x_e$  [28] according to K&P [15] is

$$E_{vib}(1) = 0.2869 \text{ eV} \quad (2314 \text{ cm}^{-1}) \quad (13.293)$$

and the experimental anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{14}\text{ND}$  [28] is

$$10 \quad \omega_0 x_0 = 42 \text{ cm}^{-1} \quad (13.294)$$

which match the predictions given by Eqs. (13.289), (13.290) and (13.291), respectively.

Using Eqs. (13.133-13.134) and the internuclear distance,  $r = 2c'$ , and reduced mass of  $^{14}\text{NH}$  given by Eqs. (13.257) and (13.277), respectively, the corresponding  $B_e$  is

$$B_e = 16.495 \text{ cm}^{-1} \quad (13.295)$$

15 The experimental  $B_e$  rotational parameter of  $^{14}\text{NH}$  is [28]

$$B_e = 16.6993 \text{ cm}^{-1} \quad (13.296)$$

Using the internuclear distance,  $r = 2c'$ , and reduced mass of  $^{14}\text{ND}$  given by Eqs. (13.257) and (13.286), respectively, the corresponding  $B_e$  is

$$B_e = 8.797 \text{ cm}^{-1} \quad (13.297)$$

20 The experimental  $B_e$  rotational parameter of  $^{14}\text{ND}$  is [28]

$$B_e = 8.7913 \text{ cm}^{-1} \quad (13.298)$$

## THE DOPPLER ENERGY TERMS OF $^{14}\text{NH}$ AND $^{14}\text{ND}$

The equations of the radiation reaction force of hydrogen and deuterium nitride are the same as those of the corresponding hydroxyl radicals with the substitution of the hydrogen and deuterium nitride parameters. Using Eqs. (11.136) and (13.140-13.141), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 3.91850 \times 10^{16} \text{ rad/s} \quad (13.299)$$

where  $b$  is given by Eq. (13.259). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 3.91850 \times 10^{16} \text{ rad/s} = 25.79224 \text{ eV} \quad (13.300)$$

5 In Eq. (11.181), substitution of the total energy of  $NH$ ,  $E_T(NH)$ , (Eq. (13.253)) for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.300) for  $\bar{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(25.79224 \text{ eV})}{m_e c^2}} = -0.31785 \text{ eV} \quad (13.301)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $NH$  due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (13.301) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of  $NH$ . Using the experimental  $^{14}NH$   $\omega_e$  of  $3282.3 \text{ cm}^{-1}$  ( $0.40696 \text{ eV}$ ) [28]

15  $\bar{E}_{osc}(^{14}NH)$  is

$$\bar{E}_{osc}(^{14}NH) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.302)$$

$$\bar{E}_{osc}(^{14}NH) = -0.31785 \text{ eV} + \frac{1}{2} (0.40696 \text{ eV}) = -0.11437 \text{ eV} \quad (13.303)$$

Using Eqs. (13.301) and the experimental  $^{14}ND$   $\omega_e$  of  $2398 \text{ cm}^{-1}$  ( $0.29732 \text{ eV}$ ) [28]

$\bar{E}_{osc}(^{14}ND)$  is

$$20 \quad \bar{E}_{osc}(^{14}ND) = -0.31785 \text{ eV} + \frac{1}{2} (0.29732 \text{ eV}) = -0.16919 \text{ eV} \quad (13.304)$$

## TOTAL AND BOND ENERGIES OF $^{14}NH$ AND $^{14}ND$

$E_{T+osc}(NH)$ , the total energy of the  $^{14}NH$  radical including the Doppler term, is given by the sum of  $E_T(NH)$  (Eq. (13.253)) and  $\bar{E}_{osc}(^{14}NH)$  given by Eq. (13.303):

$$\begin{aligned}
 E_{T+osc}(NH) &= V_e + T + V_m + V_p + E(2p \text{ shell}) + \bar{E}_{osc}(^{14}NH) \\
 &= E_T(NH) + \bar{E}_{osc}(^{14}NH)
 \end{aligned}
 \tag{13.305}$$

$$\begin{aligned}
 E_{T+osc}(NH) &= \left\{ \frac{-e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV} \right\} \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{3}{4} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2}} \right] + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \\
 &= -31.63537 \text{ eV} - 0.31785 \text{ eV} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}
 \end{aligned}
 \tag{13.306}$$

From Eqs. (13.302-13.303) and (13.305-13.306), the total energy of  $^{14}NH$  is

$$\begin{aligned}
 E_{T+osc}(NH) &= -31.63537 \text{ eV} + \bar{E}_{osc}(^{14}NH) \\
 &= -31.63537 \text{ eV} - 0.31785 \text{ eV} + \frac{1}{2} (0.40696 \text{ eV}) \\
 &= -31.74974 \text{ eV}
 \end{aligned}
 \tag{13.307}$$

where the experimental  $\omega_e$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.  $E_{T+osc}(ND)$ , the total energy of  $^{14}ND$  including the Doppler term, is given by the sum of  $E_T(ND) = E_T(NH)$  (Eq. (13.253)) and  $\bar{E}_{osc}(^{14}ND)$  given by Eq. (13.304):

$$\begin{aligned}
 E_{T+osc}(ND) &= -31.63537 \text{ eV} + \bar{E}_{osc}(^{14}ND) \\
 &= -31.63537 \text{ eV} - 0.31785 \text{ eV} + \frac{1}{2} (0.29732 \text{ eV}) \\
 &= -31.80456 \text{ eV}
 \end{aligned}
 \tag{13.308}$$

where the experimental  $\omega_e$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term. The dissociation of the bond of the hydrogen nitride forms a free hydrogen atom with one unpaired electron and a nitrogen atom with three unpaired electrons as shown in Eq. (13.246). The  $p_x$  and  $p_y$  fields cancel and the magnetic energy (Eq. (7.46) with  $r_7 = 0.93084a_0$  is subtracted due to the one component of  $E_{mag}$  given by Eq. (10.137):

$$E(\text{magnetic}) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (0.93084a_0)^3} = \frac{8\pi\mu_0 \mu_B^2}{(0.93084a_0)^3} = 0.14185 \text{ eV}
 \tag{13.309}$$

The corresponding bond dissociation energy,  $E_D$ , is given by the sum of the total energies of the nitrogen atom and the corresponding hydrogen atom minus the sum of  $E_{T+osc}(NH)$  and  $E(magnetic)$ :

$$E_D = E(^{14}N) + E(H) - E_{T+osc}(NH) - E(magnetic) \quad (13.310)$$

5  $E(^{14}N)$  is given by Eq. (13.251),  $E_D(H)$  is given by Eq. (13.154), and  $E_D(D)$  is given by Eq. (13.155). The  $^{14}NH$  bond dissociation energy,  $E_D(^{14}NH)$ , is given by Eqs. (13.154), (13.251), (13.307), and (13.309-13.310):

$$\begin{aligned} E_D(^{14}NH) &= -(14.53414 \text{ eV} + 13.59844 \text{ eV}) - (E(magnetic) + E_{T+osc}(NH)) \\ &= -28.13258 \text{ eV} - (0.14185 - 31.74974 \text{ eV}) \\ &= 3.47530 \text{ eV} \end{aligned} \quad (13.311)$$

The experimental  $^{14}NH$  bond dissociation energy from Ref. [29] and Ref. [30] is

$$10 \quad E_D(^{14}NH) = 3.42 \text{ eV} \quad (13.312)$$

$$E_D(^{14}NH) \leq 3.47 \text{ eV} \quad (13.313)$$

The  $^{14}ND$  bond dissociation energy,  $E_D(^{14}ND)$ , is given by Eqs. (13.155), (13.251), (13.308), and (13.309-13.310):

$$\begin{aligned} E_D(^{14}ND) &= -(14.53414 \text{ eV} + 13.603 \text{ eV}) - (E(magnetic) + E_{T+osc}(ND)) \\ &= -28.13714 \text{ eV} - (0.14185 - 31.80456 \text{ eV}) \\ &= 3.5256 \text{ eV} \end{aligned} \quad (13.314)$$

15 The experimental  $^{14}ND$  bond dissociation energy from Ref. [31] and Ref. [30] is

$$E_{D_{298}}(^{14}ND) \leq 339 \text{ kJ/mol} = 3.513 \text{ eV} \quad (13.315)$$

$$E_D(^{14}ND) \leq 3.54 \text{ eV} \quad (13.316)$$

The results of the determination of bond parameters of  $NH$  and  $ND$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the  
20 experimental and calculated results is excellent.

## DIHYDROGEN NITRIDE ( $NH_2$ )

The dihydrogen nitride radical  $NH_2$  is formed by the reaction of a hydrogen atom with a  
25 hydrogen nitride radical:



$NH_2$  can be solved using the same principles as those used to solve  $H_2O$ . Two diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with  
 5 two nitrogen atomic orbitals (AOs) to form the MO of  $NH_2$ . The solution is very similar to that of  $NH$  except that there are two  $NH$  bonds in  $NH_2$ .

#### FORCE BALANCE OF $NH_2$

$NH_2$  comprises two chemical bonds between nitrogen and hydrogen. Each  $N-H$   
 10 bond comprises two spin-paired electrons with one from an initially unpaired electron of the nitrogen atom and the other from the hydrogen atom. Each  $H$ -atom electron forms a  $H_2$ -type ellipsoidal MO with one of the initially unpaired  $N$ -atom electrons,  $2p_x$  or  $2p_y$ , such that the proton and the  $N$  nucleus serve as the foci. The initial  $N$  electron configuration given in the Seven-Electron Atoms section is  $1s^2 2s^2 2p^3$ , and the orbital arrangement is  
 15 given by Eqs. (10.134) and (13.246). The radius and the energy of the  $N2p$  shell are unchanged with bond formation. The central paramagnetic force due to spin of each  $N-H$  bond is provided by the spin-pairing force of the  $NH_2$  MO that has the symmetry of an  $s$  orbital that superimposes with the  $N2p$  orbitals such that the corresponding angular momenta are unchanged.

20 As in the case of  $H_2$ , each of two  $N-H$ -bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $N$  atom for distances shorter than the radius of the  $2p$  shell since it is energetically unfavorable. Thus, the MO surface comprises a prolate spheroid at each  $H$  proton that is continuous with the  $2p$  shell at the  $N$  atom. The energies in the  $NH_2$  MO involve only each  $N2p$  and each  $H1s$  electron with the  
 25 formation of each  $N-H$  bond. The sum of the energies of the prolate spheroids is matched to that of the  $2p$  shell. The forces are determined by these energies. As in the case of  $NH$ , the linear combination of each  $H_2$ -type ellipsoidal MO with each  $N2p$  AO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the  $N2p$  AO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $NH_2$  MO must comprise two

$N-H$  bonds with each comprising 75% of a  $H_2$ -type ellipsoidal MO (1/2 +25%) and a nitrogen AO:

$$[1 N2p_x AO + 0.75 H_2 MO] + [1 N2p_y AO + 0.75 H_2 MO] \rightarrow NH_2 MO \quad (13.318)$$

5

The force constant  $k'$  of the each  $H_2$ -type-ellipsoidal-MO component of the  $NH_2$  MO is given by Eq. (13.248). The distance from the origin of each  $N-H$ -bond MO to each focus  $c'$  is given by Eq. (13.249). The internuclear distance is given by Eq. (13.250). The length of the semiminor axis of the prolate spheroidal  $N-H$ -bond MO  $b=c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of each  $N-H$ -bond MO. Since each of the two prolate spheroidal  $N-H$ -bond MOs comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $N$  AO, the energy  $E$  in Eq. (13.251) adds to that of the two corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $NH_2$  MO. From the energy equation and the relationship between the axes, the dimensions of the  $NH_2$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  are twice those of  $OH$  and  $NH$  given by Eqs. (13.67-13.73) and equal to those of  $H_2O$  given by Eqs. (13.172-13.178). Similarly to  $H_2O$ , since the each prolate spheroidal  $H_2$ -type MO transitions to the  $N$  AO and the energy of the  $N2p$  shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.251), the total energy  $E_T(NH_2)$  of the  $NH_2$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $N$  AO and the two  $H_2$ -type ellipsoidal MOs that forms the  $NH_2$  MO as given by Eq. (13.318):

$$\begin{aligned} E_T(NH_2) &= E_T + E(2p \text{ shell}) \\ &= E_T - E(\text{ionization}; N) \\ &= -\frac{e^2}{4\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV} \end{aligned} \quad (13.319)$$

25

The two hydrogen atoms and the nitrogen atom can achieve an energy minimum as a linear combination of two  $H_2$ -type ellipsoidal MOs each having the proton and the nitrogen nucleus as the foci. Each  $N-H$ -bond MO comprises the same  $N2p$  shell of constant

energy given by Eq. (13.251). Thus, the energy of the  $NH_2$  MO is also given by the sum of that of the two  $H_2$ -type ellipsoidal MOs given by Eq. (11.212) minus the energy of the redundant nitrogen atom of the linear combination given by Eq. (13.251):

$$\begin{aligned} E_T(2H_2 - N) &= -2 \frac{e^2}{8\pi\epsilon_0 a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] - E(2p \text{ shell}) \\ &= 2(-31.63536831 \text{ eV}) - (-14.53414 \text{ eV}) \\ &= -48.73660 \text{ eV} \end{aligned} \quad (13.320)$$

5  $E_T(NH_2)$  given by Eq. (13.319) is set equal to two times the energy of the  $H_2$ -type ellipsoidal MO minus the energy of the  $N2p$  shell given by Eq. (13.320):

$$E_T(NH_2) = -\frac{e^2}{4\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV} = -48.73660 \text{ eV} \quad (13.321)$$

From the energy relationship given by Eq. (13.321) and the relationship between the axes  
10 given by Eqs. (13.248-13.250) and (13.62-13.63), the dimensions of the  $NH_2$  MO can be solved.

Substitution of Eq. (13.249) into Eq. (13.321) gives

$$\frac{e^2}{4\pi\epsilon_0 \sqrt{0.712154aa_0}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{0.712154aa_0}}{a - \sqrt{0.712154aa_0}} - 1 \right] = e34.20246 \quad (13.322)$$

The most convenient way to solve Eq. (13.322) is by the reiterative technique using a  
15 computer. The result to within the round-off error with five-significant figures is

$$a = 1.36276a_0 = 7.21141 \times 10^{-11} \text{ m} \quad (13.323)$$

Substitution of Eq. (13.323) into Eq. (13.249) gives

$$c' = 0.98514a_0 = 5.21312 \times 10^{-11} \text{ m} \quad (13.324)$$

The internuclear distance given by multiplying Eq. (13.324) by two is

$$2c' = 1.97027a_0 = 1.04262 \times 10^{-10} \text{ m} \quad (13.325)$$

The experimental bond distance is [32]

$$2c' = 1.024 \times 10^{-10} \text{ m} \quad (13.326)$$

Substitution of Eqs. (13.323-13.324) into Eq. (13.62) gives

$$b = c = 0.94160a_0 = 4.98276 \times 10^{-11} \text{ m} \quad (13.327)$$

25 Substitution of Eqs. (13.323-13.324) into Eq. (13.63) gives

$$e = 0.72290 \quad (13.328)$$

The nucleus of the  $H$  atom and the nucleus of the  $N$  atom comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of each  $H_2$ -type ellipsoidal MO and the  $N2p_x$  AO or  $N2p_y$  AO are given by Eqs. (13.84-13.95) and (13.261-13.270). Using Eqs. (13.323-13.325) and (13.327-13.328), the polar intersection angle  $\theta'$  given by  
 5 Eq. (13.261) with  $r_n = r_7 = 0.93084a_0$  is

$$\theta' = 114.61^\circ \quad (13.329)$$

Then, the angle  $\theta_{N2pAO}$  the radial vector of the  $N2p_x$  AO or  $N2p_y$  AO makes with the internuclear axis is

$$\theta_{N2pAO} = 180^\circ - 114.61^\circ = 65.39^\circ \quad (13.330)$$

10 as shown in Figure 10. The angle  $\theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the  $N$  radial vector given by Eqs. (13.264-13.265), (13.327), and (13.330) is

$$\theta_{H_2MO} = 64.00^\circ \quad (13.331)$$

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal  
 15 MO to the point of intersection of the orbitals given by Eqs. (13.267), (13.323), and (13.331) is

$$d_{H_2MO} = 0.59748a_0 = 3.16175 \times 10^{-11} \text{ m} \quad (13.332)$$

The distance  $d_{N2pAO}$  along the internuclear axis from the origin of the  $N$  atom to the point of intersection of the orbitals given by Eqs. (13.269), (13.324), and (13.332) is

$$20 \quad d_{N2pAO} = 0.38765a_0 = 2.05137 \times 10^{-11} \text{ m} \quad (13.333)$$

As shown in Eq. (13.318), in addition to the  $p$ -orbital charge-density modulation, the uniform charge-density in the  $p_x$  and  $p_y$  orbitals is increased by a factor of 0.25 and the  $H$  atoms are each decreased by a factor of 0.25. Using the orbital composition of  $NH_2$  (Eq. (13.318)), the radii of  $N1s = 0.14605a_0$  (Eq. (10.51)),  $N2s = 0.69385a_0$  (Eq. (10.62)), and  
 25  $N2p = 0.93084a_0$  (Eq. (10.142)) shells, and the parameters of the  $NH_2$  MO given by Eqs. (13.3-13.4) and (13.323-13.333), the charge-density of the  $NH_2$  MO comprising the linear combination of two  $N-H$ -bond MOs ( $NH$ -type ellipsoidal MOs given in the Energies of  $NH$  section) according to Eq. (13.318) is shown in Figure 12. Each  $N-H$ -bond MO



comprises a  $H_2$ -type ellipsoidal MO and an  $N2p$  AO having the dimensional diagram shown in Figure 10.

## ENERGIES OF $NH_2$

5 The energies of  $NH_2$  given by the substitution of the semiprincipal axes ((Eqs. (13.323-13.325) and (13.327)) into the energy equations (Eqs. (13.172-13.176)) are

$$V_e = \left(\frac{3}{2}\right) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -75.71422 \text{ eV} \quad (13.334)$$

$$V_p = 2 \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 27.62216 \text{ eV} \quad (13.335)$$

$$T = \left(\frac{3}{2}\right) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 27.77974 \text{ eV} \quad (13.336)$$

$$10 \quad V_m = \left(\frac{3}{2}\right) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -13.88987 \text{ eV} \quad (13.337)$$

$$E_T(NH_2) = -\frac{e^2}{4\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV} = -48.73633 \text{ eV} \quad (13.338)$$

where  $E_T(NH_2)$  is given by Eq. (13.319) which is reiteratively matched to Eq. (13.320) within five-significant-figure round-off error.

15

## VIBRATION OF $NH_2$

The vibrational energy levels of  $NH_2$  may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as

20 given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERM OF $NH_2$

The radiation reaction force in the case of the vibration of  $NH_2$  in the transition state  
25 corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) and Eqs. (13.22) and (13.144)

that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. The equations of the radiation reaction force of dihydrogen and dideuterium nitride are the same as those of the corresponding water molecules with the substitution of the dihydrogen and dideuterium  
 5 nitride parameters. Using Eqs. (11.136) and (13.207-13.209), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\left(\frac{3}{2}\right) \frac{e^2}{4\pi\epsilon_0 b^3}}{m_e}} = 5.54150 \times 10^{16} \text{ rad/s} \quad (13.339)$$

where  $b$  is given by Eq. (13.327). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$10 \quad \bar{E}_K = \hbar\omega = \hbar 5.54150 \times 10^{16} \text{ rad/s} = 36.47512 \text{ eV} \quad (13.340)$$

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.340) for  $\bar{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

$$15 \quad \bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(36.47512 \text{ eV})}{m_e c^2}} = -0.37798 \text{ eV} \quad (13.341)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $NH_2$  due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by  
 20 Eq. (13.341) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of  $NH_2$ . Using the experimental  $^{14}NH_2$  vibrational energy of  $E_{vib} = 3301.110 \text{ cm}^{-1} = 0.40929 \text{ eV}$  [33] gives

$$\bar{E}'_{osc} = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.342)$$

$$\bar{E}'_{osc} = -0.37798 \text{ eV} + \frac{1}{2} (0.40929 \text{ eV}) = -0.17334 \text{ eV} \quad (13.343)$$

25 per bond. As in the case for  $H_2O$ , the reentrant orbit for the binding of a hydrogen atom to a  $NH$  radical causes the bonds to oscillate by increasing and decreasing in length along the

two  $N-H$  bonds at a relative phase angle of  $180^\circ$ . Since the vibration and reentrant oscillation is along two bonds for the asymmetrical stretch ( $\nu_3$ ),  $\bar{E}_{osc}$  for  $^{14}NH_2$ ,  $\bar{E}_{osc}(^{14}NH_2)$ , is:

$$\begin{aligned}\bar{E}_{osc}(^{14}NH_2) &= 2\left(\bar{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \\ &= 2\left(-0.37798 \text{ eV} + \frac{1}{2}(0.40929 \text{ eV})\right) \\ &= -0.34668 \text{ eV}\end{aligned}\quad (13.344)$$

5 Using Eq. (13.341), Eqs. (13.342-13.344), and the  $^{14}ND_2$  vibrational energy of  $E_{vib} = 2410.79 \text{ cm}^{-1} = 0.29890 \text{ eV}$ , calculated from the experimental  $^{14}NH_2$  vibrational energy using Eq. (11.148), the corresponding  $\bar{E}_{osc}(^{14}ND_2)$  is

$$\begin{aligned}\bar{E}_{osc}(^{14}ND_2) &= 2\left(-0.37798 \text{ eV} + \frac{1}{2}(0.29890 \text{ eV})\right) \\ &= -0.45707 \text{ eV}\end{aligned}\quad (13.345)$$

## 10 TOTAL AND BOND ENERGIES OF $^{14}NH_2$ AND $^{14}ND_2$

$E_{T+osc}(^{14}NH_2)$ , the total energy of the  $^{14}NH_2$  including the Doppler term, is given by the sum of  $E_T(NH_2)$  (Eq. (13.321)) and  $\bar{E}_{osc}(^{14}NH_2)$  given Eqs. (13.339-13.344):

$$\begin{aligned}E_{T+osc}(^{14}NH_2) &= V_e + T + V_m + V_p + E(N2p) + \bar{E}_{osc}(^{14}NH_2) \\ &= E_T(NH_2) + \bar{E}_{osc}(^{14}NH_2)\end{aligned}\quad (13.346)$$

$$\begin{aligned}E_{T+osc}(^{14}NH_2) &= \left\{ \left( \frac{-e^2}{4\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV} \right) \right. \\ &\quad \left. - 2 \left( (31.63536831 \text{ eV}) \sqrt{\frac{2\hbar \sqrt{\frac{3}{2} \frac{e^2}{4\pi\epsilon_0 b^3}} m_e}{m_e c^2}} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \right\} \\ &= -48.73660 \text{ eV} - 2 \left( 0.37798 \text{ eV} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)\end{aligned}\quad (13.347)$$

15 From Eqs. (13.344) and (13.346-13.347), the total energy of  $^{14}NH_2$  is

$$\begin{aligned}
E_{T+osc}({}^{14}\text{NH}_2) &= -48.73660 \text{ eV} + \bar{E}_{osc}({}^{14}\text{NH}_2) \\
&= -48.73660 \text{ eV} - 2 \left( 0.37798 \text{ eV} - \frac{1}{2} (0.40929 \text{ eV}) \right) \\
&= -49.08328 \text{ eV}
\end{aligned} \tag{13.348}$$

where the experimental  ${}^{14}\text{NH}_2$  vibrational energy was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

$E_{T+osc}({}^{14}\text{ND}_2)$ , the total energy of  ${}^{14}\text{ND}_2$  including the Doppler term is given by the sum of  $E_T(\text{ND}_2) = E_T(\text{NH}_2)$  (Eq. (13.321)) and  $\bar{E}_{osc}({}^{14}\text{ND}_2)$  given by Eq. (13.345):

$$\begin{aligned}
E_{T+osc}({}^{14}\text{ND}_2) &= -48.73660 \text{ eV} + \bar{E}_{osc}({}^{14}\text{ND}_2) \\
&= -48.73660 \text{ eV} - 2 \left( 0.37798 \text{ eV} - \frac{1}{2} (0.29890 \text{ eV}) \right) \\
&= -49.19366 \text{ eV}
\end{aligned} \tag{13.349}$$

where the experimental  ${}^{14}\text{NH}_2$  vibrational energy corrected for the reduced mass difference

of hydrogen and deuterium was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term. The corresponding bond

dissociation energy,  $E_D$ , is given by the sum of the total energies of the corresponding

hydrogen nitride radical and hydrogen atom minus the total energy of dihydrogen nitride,

$$E_{T+osc}({}^{14}\text{NH}_2).$$

Thus,  $E_D$  of  ${}^{14}\text{NH}_2$  is given by:

$$E_D({}^{14}\text{NH}_2) = E(\text{H}) + E({}^{14}\text{NH}) - E_{T+osc}({}^{14}\text{NH}_2) \tag{13.350}$$

where  $E_T({}^{14}\text{NH})$  is given by the of the sum of the experimental energies of  ${}^{14}\text{N}$  (Eq. (13.251)),  $\text{H}$  (Eq. (13.154)), and the negative of the bond energy of  ${}^{14}\text{NH}$  (Eq. (13.312)):

$$E({}^{14}\text{NH}) = -13.59844 \text{ eV} - 14.53414 \text{ eV} - 3.42 \text{ eV} = -31.55258 \text{ eV} \tag{13.351}$$

From Eqs. (13.154), (13.348), and (13.350-13.351),  $E_D({}^{14}\text{NH}_2)$  is

$$\begin{aligned}
E_D({}^{14}\text{NH}_2) &= E(\text{H}) + E({}^{14}\text{NH}) - E_{T+osc}({}^{14}\text{NH}_2) \\
&= -13.59844 \text{ eV} - 31.55258 \text{ eV} - (-49.08328 \text{ eV}) \\
&= 3.9323 \text{ eV}
\end{aligned} \tag{13.352}$$

The experimental  ${}^{14}\text{NH}_2$  bond dissociation energy from Ref. [34] and Ref. [35] is

$$E_D({}^{14}\text{NH}_2) = 88 \pm 4 \text{ kcal / mole} = 3.8160 \text{ eV} \tag{13.353}$$

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$$E_D(^{14}\text{NH}_2) = 91.0 \pm 0.5 \text{ kcal/mole} = 3.9461 \text{ eV} \quad (13.354)$$

Similarly,  $E_D$  of  $^{14}\text{ND}_2$  is given by:

$$E_D(^{14}\text{ND}_2) = E(D) + E(^{14}\text{ND}) - (E_{T+osc}(^{14}\text{ND}_2)) \quad (13.355)$$

where  $E_T(^{14}\text{ND})$  is given by the of the sum of the experimental energies of  $^{14}\text{N}$  (Eq. 5 (13.251)),  $D$  (Eq. (13.155)), and the negative of the bond energy of  $^{14}\text{ND}$  (Eq. (13.315)):

$$E(^{14}\text{ND}) = -13.603 \text{ eV} - 14.53414 \text{ eV} - 3.513 \text{ eV} = -31.6506 \text{ eV} \quad (13.356)$$

From Eqs. (13.155), (13.349), and (13.355-13.356),  $E_D(^{14}\text{ND}_2)$  is

$$\begin{aligned} E_D(^{14}\text{ND}_2) &= -13.603 \text{ eV} - 31.6506 \text{ eV} - (-49.19366 \text{ eV}) \\ &= 3.9401 \text{ eV} \end{aligned} \quad (13.357)$$

The  $^{14}\text{ND}_2$  bond dissociation energy calculated from the average of the experimental bond 10 energies [34-35] and vibrational energy of  $^{14}\text{NH}_2$  [33] is

$$\begin{aligned} E_D(^{14}\text{ND}_2) &= E_D(^{14}\text{NH}_2) + \frac{1}{2}(E_{vib}(^{14}\text{NH}_2) - E_{vib}(^{14}\text{ND}_2)) \\ &= \frac{1}{2}(3.8160 \text{ eV} + 3.9461 \text{ eV}) + \frac{1}{2}(0.40929 \text{ eV} - 0.29890 \text{ eV}) \\ &= 3.9362 \text{ eV} \end{aligned} \quad (13.358)$$

## BOND ANGLE OF $\text{NH}_2$

The  $\text{NH}_2$  MO comprises a linear combination of two  $\text{N}-\text{H}$ -bond MOs. Each  $\text{N}-\text{H}$ -bond 15 MO comprises the superposition of a  $\text{H}_2$ -type ellipsoidal MO and the  $\text{N}2p_x$  AO or the  $\text{N}2p_y$  AO with a relative charge density of 0.75 to 1.25; otherwise, the  $\text{N}2p$  AOs are the same as those of the nitrogen atom. A bond is also possible between the two H atoms of the  $\text{N}-\text{H}$  bonds. Such  $\text{H}-\text{H}$  bonding would decrease the  $\text{N}-\text{H}$  bond strength since electron density would be shifted from the  $\text{N}-\text{H}$  bonds to the  $\text{H}-\text{H}$  bond. Thus, the bond 20 angle between the two  $\text{N}-\text{H}$  bonds is determined by the condition that the total energy of the  $\text{H}_2$ -type ellipsoidal MO between the terminal H atoms of the  $\text{N}-\text{H}$  bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the  $\text{H}-\text{H}$  ellipsoidal MO is

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \quad (13.359)$$

The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \quad (13.360)$$

The length of the semiminor axis of the prolate spheroidal  $H-H$  MO  $b=c$  is given by Eq. (13.167).

- 5 Since the two  $H_2$ -type ellipsoidal MOs comprise 75% of the  $H$  electron density of  $H_2$  and the energy of each  $H_2$ -type ellipsoidal MO is matched to that of the  $N2p$  AO; the component energies and the total energy  $E_T$  of the  $H-H$  bond are given by Eqs. (13.67-13.73) except that  $V_e$ ,  $T$ , and  $V_m$  are corrected for the energy matching factor of 0.93613 given in Eq. (13.248). Substitution of Eq. (13.359) into Eq. (13.233) with the energy-
- 10 matching factor gives

$$0 = \left[ \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left[ (0.93613)^{-1} \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{\frac{0.75e^2}{4\pi\epsilon_0 a^3}}{m_e c^2}} \right] \right. \\ \left. + \frac{1}{2} \hbar \sqrt{\frac{\frac{0.75e^2}{8\pi\epsilon_0 a^3} - \frac{e^2}{8\pi\epsilon_0 (a+c')^3}}{0.5m_p}} \right] \quad (13.361)$$

From the energy relationship given by Eq. (13.361) and the relationship between the axes given by Eqs. (13.359-13.360) and (13.167-13.168), the dimensions of the  $H-H$  MO can

15 be solved.

The most convenient way to solve Eq. (13.361) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 4.9500a_0 = 2.6194 \times 10^{-10} \text{ m} \quad (13.362)$$

Substitution of Eq. (13.362) into Eq. (13.359) gives

$$20 \quad c' = 1.5732a_0 = 8.3251 \times 10^{-11} \text{ m} \quad (13.363)$$

The internuclear distance given by multiplying Eq. (13.363) by two is

$$2c' = 3.1464a_0 = 1.6650 \times 10^{-10} \text{ m} \quad (13.364)$$

Substitution of Eqs. (13.362-13.363) into Eq. (13.167) gives

$$b = c = 4.6933a_0 = 2.4836 \times 10^{-10} \text{ m} \quad (13.365)$$

25 Substitution of Eqs. (13.362-13.363) into Eq. (13.168) gives

$$e = 0.3178 \quad (13.366)$$

Using,  $2c'_{H-H}$  (Eq. (13.364)), the distance between the two  $H$  atoms when the total energy of the corresponding MO is zero (Eq. (13.361)), and  $2c'_{N-H}$  (Eq. (13.325)), the internuclear distance of each  $N-H$  bond, the corresponding bond angle can be determined  
 5 from the law of cosines. Using, Eq. (13.242), the bond angle  $\theta$  between the  $N-H$  bonds is

$$\begin{aligned} \theta &= \cos^{-1} \left( \frac{2(1.9703)^2 - (3.1464)^2}{2(1.9703)^2} \right) \\ &= \cos^{-1}(-0.2751) = 105.969^\circ \end{aligned} \quad (13.367)$$

The experimental angle between the  $N-H$  bonds is [32]

$$\theta = 103.3^\circ \quad (13.368)$$

The results of the determination of bond parameters of  $NH_2$  and  $ND_2$  are given in  
 10 Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

### AMMONIA ( $NH_3$ )

15 Ammonia ( $NH_3$ ) is formed by the reaction of a hydrogen atom with a dihydrogen nitride radical:



$NH_3$  can be solved using the same principles as those used to solve  $NH_2$  except that three rather than two  $H_2$ -type prolate spheroidal molecular orbitals (MOs) serve as basis functions  
 20 in a linear combination with nitrogen atomic orbitals (AOs) to form the MO of  $NH_3$ .

### FORCE BALANCE OF $NH_3$

$NH_3$  comprises three chemical bonds between nitrogen and hydrogen. Each  $N-H$  bond comprises two spin-paired electrons with one from an initially unpaired electron of the  
 25 nitrogen atom and the other from the hydrogen atom. Each  $H$ -atom electron forms a  $H_2$ -type ellipsoidal MO with one of the initially unpaired  $N$ -atom electrons,  $2p_x$ ,  $2p_y$ , or  $2p_z$ , such that the proton and the  $N$  nucleus serve as the foci. The initial  $N$  electron configuration given in the Seven-Electron Atoms section is  $1s^2 2s^2 2p^3$ , and the orbital

arrangement is given by Eqs. (10.134) and (13.246). The radius and the energy of the  $N2p$  shell are unchanged with bond formation. The central paramagnetic force due to spin of each  $N-H$  bond is provided by the spin-pairing force of the  $NH_3$  MO that has the symmetry of an  $s$  orbital that superimposes with the  $N2p$  orbitals such that the corresponding angular  
5 momenta are unchanged.

As in the case of  $H_2$ , each of three  $N-H$ -bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the  $N$  atom for distances shorter than the radius of the  $2p$  shell since it is energetically unfavorable. Thus, the MO surface comprises a prolate spheroid at each  $H$  proton that is continuous with the  $2p$  shell at  
10 the  $N$  atom. The energies in the  $NH_3$  MO involve only each  $N2p$  and each  $H1s$  electron with the formation of each  $N-H$  bond. The sum of the energies of the prolate spheroids is matched to that of the  $2p$  shell. The forces are determined by these energies. As in the cases of  $NH$  and  $NH_2$ , the linear combination of each  $H_2$ -type ellipsoidal MO with each  $N2p$  AO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the  $N2p$   
15 AO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $NH_3$  MO must comprise three  $N-H$  bonds with each comprising 75% of a  $H_2$ -type ellipsoidal MO (1/2 +25%) and a nitrogen AO:

$$[1 N2p_x AO + 0.75 H_2 MO] + [1 N2p_y AO + 0.75 H_2 MO] + [1 N2p_z AO + 0.75 H_2 MO] \\ \rightarrow NH_3 MO$$

(13.370)

20 The force constant  $k'$  of the each  $H_2$ -type-ellipsoidal-MO component of the  $NH_3$  MO is given by Eq. (13.248). The distance from the origin of each  $N-H$ -bond MO to each focus  $c'$  is given by Eq. (13.249). The internuclear distance is given by Eq. (13.250). The length of the semiminor axis of the prolate spheroidal  $N-H$ -bond MO  $b = c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$   
25 then allows for the solution of the other axes of each prolate spheroid and eccentricity of each  $N-H$ -bond MO. Since each of the three prolate spheroidal  $N-H$ -bond MOs comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $N$  AO, the energy  $E$  in Eq. (13.251) adds to that of the three corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $NH_3$



MO. From the energy equation and the relationship between the axes, the dimensions of the  $NH_3$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  are three times those of  $OH$  and  $NH$  given by Eqs. (13.67-13.73) and 1.5 times those of  $H_2O$  given by Eqs. (13.172-13.178).

5 Similarly to  $H_2O$ , since the each prolate spheroidal  $H_2$ -type MO transitions to the  $N$  AO and the energy of the  $N2p$  shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.251), the total energy  $E_T(NH_3)$  of the  $NH_3$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $N$  AO and the three  $H_2$ -type ellipsoidal MOs that forms the  $NH_3$  MO as  
10 given by Eq. (13.370):

$$\begin{aligned} E_T(NH_3) &= E_T + E(2p \text{ shell}) \\ &= E_T - E(\text{ionization}; N) \\ &= -3 \frac{e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV} \end{aligned} \quad (13.371)$$

The three hydrogen atoms and the nitrogen atom can achieve an energy minimum as a linear combination of three  $H_2$ -type ellipsoidal MOs each having the proton and the nitrogen nucleus as the foci. Each  $N-H$ -bond MO comprises the same  $N2p$  shell of constant  
15 energy given by Eq. (13.251). Thus, an energy term of the  $NH_3$  MO is given by the sum of the three  $H_2$ -type ellipsoidal MOs given by Eq. (11.212) minus the energy of the redundant nitrogen atom of the linear combination given by Eq. (13.251). The total sum is determined by the energy matching condition of the binding atoms.

In Eq. (13.248), the equipotential condition of the union of each  $H_2$ -type-ellipsoidal-  
20 MO and the  $N$  AO was met when the force constant used to determine the ellipsoidal parameter  $c'$  was normalized by the ratio of the ionization energy of  $N$  14.53414 eV [6] and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). This normalized the force to match that of the Coulombic force alone to meet the force matching condition of the  $NH$  MO under the influence of the proton  
25 and the  $N$  nucleus. The minimum total energy of the  $NH_3$  MO from the sum of energies of a linear combination from four atoms is determined using the energy matching condition of Eq. (13.248). Since each of the three prolate spheroidal  $N-H$ -bond MOs of  $NH_3$  comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $N$  AO and the energy matching

condition is met, the nitrogen energy  $E$  (Eq. (13.251)) and the energy (Eq. (1.243)) of a hydrogen atomic orbital ( $H$  AO),  $E_{Coulomb}(H)$ , corresponding to the Coulombic force of  $+e$  from the nitrogen nucleus is subtracted from the sum of the energies of the three corresponding  $H_2$ -type ellipsoidal MOs to given an energy minimum. From another perspective, the electron configuration of  $NH_2$  is equivalent to that of  $OH$  and is given by Eq. (10.174).  $NH_2$  serves as a one-electron atom that is energy matched by the  $H$  AO as a basis element to minimize the energy of  $NH_3$  in the formation of the third  $N-H$ -bond.

$$E_T(3H_2 - N - H) = \left\{ -3 \frac{e^2}{8\pi\epsilon_0 a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] \right. \\ \left. - E(N2p \text{ shell}) - E_{Coulomb}(H) \right\} \\ = 3(-31.63536831 \text{ eV}) - (-14.53414 \text{ eV} - 13.605804 \text{ eV}) \quad (13.372) \\ = -66.76616 \text{ eV}$$

$E_T(NH_3)$  given by Eq. (13.371) is set equal to Eq. (13.372), three times the energy of the  $H_2$ -type ellipsoidal MO minus the energy of the  $N2p$  shell and the  $H$  AO:

$$E_T(NH_3) = -3 \frac{e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV} = -66.76616 \text{ eV} \quad (13.373)$$

From the energy relationship given by Eq. (13.373) and the relationship between the axes given by Eqs. (13.248-13.250) and (13.62-13.63), the dimensions of the  $NH_3$  MO can be solved.

Substitution of Eq. (13.249) into Eq. (13.373) gives

$$\frac{3e^2}{8\pi\epsilon_0 \sqrt{0.712154aa_0}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{0.712154aa_0}}{a - \sqrt{0.712154aa_0}} - 1 \right] = e52.23202 \quad (13.374)$$

The most convenient way to solve Eq. (13.374) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.34750a_0 = 7.13066 \times 10^{-11} \text{ m} \quad (13.375)$$

Substitution of Eq. (13.375) into Eq. (13.249) gives

$$c' = 0.97961a_0 = 5.18385 \times 10^{-11} \text{ m} \quad (13.376)$$

The internuclear distance given by multiplying Eq. (13.376) by two is

$$2c' = 1.95921a_0 = 1.03677 \times 10^{-10} \text{ m} \quad (13.377)$$

The experimental bond distance is [32]

$$2c' = 1.012 \times 10^{-10} \text{ m} \quad (13.378)$$

Substitution of Eqs. (13.375-13.376) into Eq. (13.62) gives

$$b = c = 0.92527a_0 = 4.89633 \times 10^{-11} \text{ m} \quad (13.379)$$

5 Substitution of Eqs. (13.375-13.376) into Eq. (13.63) gives

$$e = 0.72698 \quad (13.380)$$

The nucleus of the  $H$  atom and the nucleus of the  $N$  atom comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of each  $H_2$ -type ellipsoidal MO and the  $N2p_x$ ,  $N2p_y$ , or  $N2p_z$  AO are given by Eqs. (13.84-13.95), (13.261-13.270), and  
 10 (13.261-13.270). Using Eqs. (13.375-13.377) and (13.379-13.380), the polar intersection angle  $\theta'$  given by Eq. (13.261) with  $r_n = r_7 = 0.93084a_0$  is

$$\theta' = 115.89^\circ \quad (13.381)$$

Then, the angle  $\theta_{N2pAO}$  the radial vector of the  $N2p_x$ ,  $N2p_y$ , or  $N2p_z$  AO makes with the internuclear axis is

$$15 \quad \theta_{N2pAO} = 180^\circ - 115.89^\circ = 64.11^\circ \quad (13.382)$$

as shown in Figure 10. The angle  $\theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the  $N$  radial vector given by Eqs. (13.264-13.265), (13.379), and (13.382) is

$$\theta_{H_2MO} = 64.83^\circ \quad (13.383)$$

20 Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.267), (13.375), and (13.383) is

$$d_{H_2MO} = 0.57314a_0 = 3.03292 \times 10^{-11} \text{ m} \quad (13.384)$$

The distance  $d_{N2pAO}$  along the internuclear axis from the origin of the  $N$  atom to the point of  
 25 intersection of the orbitals given by Eqs. (13.269), (13.376), and (13.384) is

$$d_{N2pAO} = 0.40647a_0 = 2.15093 \times 10^{-11} \text{ m} \quad (13.385)$$

As shown in Eq. (13.370), in addition to the  $p$ -orbital charge-density modulation, the uniform charge-density in the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals is increased by a factor of 0.25 and the  $H$  atoms are each decreased by a factor of 0.25. Using the orbital composition of  $NH_3$  (Eq.

(13.370)), the radii of  $N1s = 0.14605a_0$  (Eq. (10.51)),  $N2s = 0.69385a_0$  (Eq. (10.62)), and  $N2p = 0.93084a_0$  (Eq. (10.142)) shells, and the parameters of the  $NH_3$  MO given by Eqs. (13.3-13.4) and (13.375-13.385), the charge-density of the  $NH_3$  MO comprising the linear combination of three  $N-H$ -bond MOs ( $NH$ -type ellipsoidal MOs given in the Energies of  $NH$  section) according to Eq. (13.370) is shown in Figure 13. Each  $N-H$ -bond MO comprises a  $H_2$ -type ellipsoidal MO and an  $N2p$  AO having the dimensional diagram shown in Figure 10.

### ENERGIES OF $NH_3$

10 The energies of  $NH_3$  given by the substitution of the semiprincipal axes ((Eqs. (13.375-13.377) and (13.379)) into the energy equations (Eqs. (13.67-13.73)) multiplied by three are

$$V_e = 3 \left( \frac{3}{4} \right) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -115.28799 \text{ eV} \quad (13.386)$$

$$V_p = 3 \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 41.66718 \text{ eV} \quad (13.387)$$

$$T = 3 \left( \frac{3}{4} \right) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 42.77848 \text{ eV} \quad (13.388)$$

$$15 \quad V_m = 3 \left( \frac{3}{4} \right) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -21.38924 \text{ eV} \quad (13.389)$$

$$E_T(NH_3) = -3 \frac{e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV} = -66.76571 \text{ eV} \quad (13.390)$$

where  $E_T(NH_3)$  is given by Eq. (13.371) which is reiteratively matched to Eq. (13.372) within five-significant-figure round-off error.

20

### VIBRATION OF $NH_3$

The vibrational energy levels of  $NH_3$  may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as

given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

### THE DOPPLER ENERGY TERM OF $NH_3$

- 5 The radiation reaction force in the case of the vibration of  $NH_3$  in the transition state corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) and Eqs. (13.22) and (13.144) that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. The equations of the radiation reaction force of ammonia are the same as those of the corresponding water and
- 10 dihydrogen and dideuterium nitride radicals with the substitution of the ammonia parameters. Using Eqs. (11.136) and (13.207-13.209), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\left(\frac{3}{2}\right) \frac{e^2}{4\pi\epsilon_0 b^3}}{m_e}} = 5.68887 \times 10^{16} \text{ rad/s} \quad (13.391)$$

- where  $b$  is given by Eq. (13.379). The kinetic energy,  $E_K$ , is given by Planck's equation
- 15 (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 5.68887 \times 10^{16} \text{ rad/s} = 37.44514 \text{ eV} \quad (13.392)$$

- In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO acting independently due to the  $D_{3h}$  symmetry point group, for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.392) for
- 20  $\bar{E}_K$  gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.6353683 \text{ eV} \sqrt{\frac{2e(37.44514 \text{ eV})}{m_e c^2}} = -0.38298 \text{ eV} \quad (13.393)$$

- In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $NH_3$  due to
- 25 the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (13.393) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational

energy of  $NH_3$ . Using the experimental  $^{14}NH_3$  vibrational energy of  $E_{vib} = 3443.59 \text{ cm}^{-1} = 0.426954 \text{ eV}$  [36] gives

$$\bar{E}'_{osc} = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.394)$$

$$\bar{E}'_{osc} = -0.38298 \text{ eV} + \frac{1}{2} (0.426954 \text{ eV}) = -0.16950 \text{ eV} \quad (13.395)$$

5 per bond. The reentrant orbit for the binding of a hydrogen atom to a  $NH_2$  radical involves three  $N-H$  bonds. Since the vibration and reentrant oscillation is along three bonds,  $\bar{E}_{osc}$  for  $^{14}NH_3$ ,  $\bar{E}_{osc}(^{14}NH_3)$ , is:

$$\begin{aligned} \bar{E}_{osc}(^{14}NH_3) &= 3 \left( \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \\ &= 3 \left( -0.38298 \text{ eV} + \frac{1}{2} (0.426954 \text{ eV}) \right) \\ &= -0.50850 \text{ eV} \end{aligned} \quad (13.396)$$

Using Eq. (13.393), Eqs. (13.394-13.396), and the  $^{14}ND_3$  experimental vibrational  
10 energy of  $E_{vib} = 2563.96 \text{ cm}^{-1} = 0.317893 \text{ eV}$  [36], the corresponding  $\bar{E}_{osc}(^{14}ND_3)$  is

$$\begin{aligned} \bar{E}_{osc}(^{14}ND_3) &= 3 \left( -0.38298 \text{ eV} + \frac{1}{2} (0.317893 \text{ eV}) \right) \\ &= -0.67209 \text{ eV} \end{aligned} \quad (13.397)$$

### TOTAL AND BOND ENERGIES OF $^{14}NH_3$ AND $^{14}ND_3$

$E_{T+osc}(^{14}NH_3)$ , the total energy of the  $^{14}NH_3$  including the Doppler term, is given by the sum  
15 of  $E_T(NH_3)$  (Eq. (13.373)) and  $\bar{E}_{osc}(^{14}NH_3)$  given Eqs. (13.391-13.396):

$$\begin{aligned} E_{T+osc}(^{14}NH_3) &= V_e + T + V_m + V_p + E(N2p) + \bar{E}_{osc}(^{14}NH_3) \\ &= E_T(NH_3) + \bar{E}_{osc}(^{14}NH_3) \end{aligned} \quad (13.398)$$

$$E_{T+osc}({}^{14}\text{NH}_3) = \left\{ \begin{aligned} & \left( 3 \frac{-e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV} \right) \\ & - 3 \left( (31.63536831 \text{ eV}) \sqrt{\frac{2\hbar \sqrt{\frac{3}{2} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2}} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \end{aligned} \right\} \quad (13.399)$$

$$= -66.76616 \text{ eV} - 3 \left( 0.38298 \text{ eV} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$

From Eqs. (13.396) and (13.398-13.399), the total energy of  ${}^{14}\text{NH}_2$  is

$$\begin{aligned} E_{T+osc}({}^{14}\text{NH}_3) &= -66.76616 \text{ eV} + \bar{E}_{osc}({}^{14}\text{NH}_3) \\ &= -66.76616 \text{ eV} - 3 \left( 0.38298 \text{ eV} - \frac{1}{2} (0.426954 \text{ eV}) \right) \\ &= -67.27466 \text{ eV} \end{aligned} \quad (13.400)$$

where the experimental  ${}^{14}\text{NH}_3$  vibrational energy was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

5  $E_{T+osc}({}^{14}\text{ND}_3)$ , the total energy of  ${}^{14}\text{ND}_3$  including the Doppler term is given by the sum of  $E_T(\text{ND}_3) = E_T(\text{NH}_3)$  (Eq. (13.373)) and  $\bar{E}_{osc}({}^{14}\text{ND}_3)$  given by Eq. (13.397):

$$\begin{aligned} E_{T+osc}({}^{14}\text{ND}_3) &= -66.76616 \text{ eV} + \bar{E}_{osc}({}^{14}\text{ND}_3) \\ &= -66.76616 \text{ eV} - 3 \left( 0.38298 \text{ eV} - \frac{1}{2} (0.317893 \text{ eV}) \right) \\ &= -67.43780 \text{ eV} \end{aligned} \quad (13.401)$$

where the experimental  ${}^{14}\text{ND}_3$  vibrational energy was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term. The

corresponding bond dissociation energy,  $E_D$ , is given by the sum of the total energies of the  
10 corresponding dihydrogen nitride radical and hydrogen atom minus the total energy of ammonia,  $E_{T+osc}({}^{14}\text{NH}_3)$ .

Thus,  $E_D$  of  ${}^{14}\text{NH}_3$  is given by:

$$E_D({}^{14}\text{NH}_3) = E(\text{H}) + E({}^{14}\text{NH}_2) - E_{T+osc}({}^{14}\text{NH}_3) \quad (13.402)$$

where  $E_T({}^{14}\text{NH}_2)$  is given by the of the sum of the experimental energies of  ${}^{14}\text{N}$  (Eq.  
15 (13.251)), two  $\text{H}$  (Eq. (13.154)), and the negative of the bond energies of  ${}^{14}\text{NH}$  (Eq. (13.312)) and  ${}^{14}\text{NH}_2$  (Eq. (13.354)):

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$$E(^{14}\text{NH}_2) = 2(-13.59844 \text{ eV}) - 14.53414 \text{ eV} - 3.42 \text{ eV} - 3.946 \text{ eV} = -49.09709 \text{ eV} \quad (13.403)$$

From Eqs. (13.154), (13.400), and (13.402-13.403),  $E_D(^{14}\text{NH}_2)$  is

$$\begin{aligned} E_D(^{14}\text{NH}_3) &= E(H) + E(^{14}\text{NH}_2) - E_{T+\text{osc}}(^{14}\text{NH}_3) \\ &= -13.59844 \text{ eV} - 49.09709 \text{ eV} - (-67.27466 \text{ eV}) \\ &= 4.57913 \text{ eV} \end{aligned} \quad (13.404)$$

5 The experimental  $^{14}\text{NH}_3$  bond dissociation energy [37] is

$$E_D(^{14}\text{NH}_3) = 4.60155 \text{ eV} \quad (13.405)$$

Similarly,  $E_D$  of  $^{14}\text{ND}_3$  is given by:

$$E_D(^{14}\text{ND}_3) = E(D) + E(^{14}\text{ND}_2) - (E_{T+\text{osc}}(^{14}\text{ND}_3)) \quad (13.406)$$

where  $E_T(^{14}\text{ND}_2)$  is given by the of the sum of the experimental energies of  $^{14}\text{N}$  (Eq. 10 (13.251)), two times the energy of  $D$  (Eq. (13.155)), and the negative of the bond energies of  $^{14}\text{ND}$  (Eq. (13.315)) and  $^{14}\text{ND}_2$  (Eq. (13.358)):

$$E(^{14}\text{ND}_2) = 2(-13.603 \text{ eV}) - 14.53414 \text{ eV} - 3.5134 \text{ eV} - 3.9362 \text{ eV} = -49.18981 \text{ eV} \quad (13.407)$$

From Eqs. (13.155), (13.401), and (13.406-13.407),  $E_D(^{14}\text{ND}_3)$  is

$$15 \quad E_D(^{14}\text{ND}_3) = -13.603 \text{ eV} - 49.18981 \text{ eV} - (-67.43780 \text{ eV}) = 4.64499 \text{ eV} \quad (13.408)$$

The experimental  $^{14}\text{ND}_3$  bond dissociation energy [37] is

$$E_D(^{14}\text{ND}_3) = 4.71252 \text{ eV} \quad (13.409)$$

### BOND ANGLE OF $\text{NH}_3$

20 Using,  $2c'_{H-H}$  (Eq. (13.364)), the distance between the two  $H$  atoms when the total energy of the corresponding MO is zero (Eq. (13.361)), and  $2c'_{N-H}$ , the internuclear distance of each  $N-H$  bond (Eq. (13.377)), the corresponding bond angle can be determined from the law of cosines. Using Eq. (13.367), the bond angle  $\theta$  between the  $N-H$  bonds is

$$\theta = \cos^{-1} \left( \frac{2(1.95921)^2 - (3.14643)^2}{2(1.95921)^2} \right) = \cos^{-1}(-0.28956) = 106.67^\circ \quad (13.410)$$

25 The experimental angle between the  $N-H$  bonds is [36]



$$\theta = 106.67^\circ \quad (13.411)$$

The  $NH_3$  molecule has a pyramidal structure with the nitrogen atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. Since any two  $N-H$  bonds form an isosceles triangle, the distance  $d_{origin-H}$  from the origin to the nucleus of a hydrogen atom is given by

$$d_{origin-H} = \frac{2c'_{H-H}}{2 \sin 60^\circ} \quad (13.412)$$

Substitution of Eq. (13.364) into Eq. (13.412) gives

$$d_{origin-H} = 1.81659a_0 \quad (13.413)$$

The height along the z-axis of the pyramid from the origin to  $N$  nucleus  $d_{height}$  is given by

$$d_{height} = \sqrt{(2c'_{N-H})^2 - (d_{origin-H})^2} \quad (13.414)$$

Substitution of Eqs. (13.377) and (13.413) into Eq. (13.414) gives

$$d_{height} = 0.73383a_0 \quad (13.415)$$

The angle  $\theta_v$  of each  $N-H$  bond from the z-axis is given by

$$\theta_v = \tan^{-1} \left( \frac{d_{origin-H}}{d_{height}} \right) \quad (13.416)$$

Substitution of Eqs. (13.413) and (13.415) into Eq. (13.417) gives

$$\theta_v = 68.00^\circ \quad (13.417)$$

The  $NH_3$  MO shown in Figure 13 was rendered using these parameters.

The results of the determination of bond parameters of  $NH_3$  and  $ND_3$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## HYDROGEN CARBIDE ( $CH$ )

The methane molecule can be solved by first considering the solution of the hydrogen carbide, dihydrogen carbide, and methyl radicals. The former is formed by the reaction of a hydrogen atom and a carbon atom:



The hydrogen carbide radicals,  $CH$  and  $CH_2$ , methyl radical,  $CH_3$ , and methane,  $CH_4$ , can be solved using the same principles as those used to solve  $OH$ ,  $H_2O$ ,  $NH$ ,  $NH_2$ , and  $NH_3$  with the exception that the carbon  $2s$  and  $2p$  shells hybridize to form a single  $2sp^3$  shell as an energy minimum.

5

### FORCE BALANCE OF $CH$

$CH$  comprises two spin-paired electrons in a chemical bond between the carbon atom and the hydrogen atom. The  $CH$  radical molecular orbital (MO) is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal  $H_2$  MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, the  $H$ -atom electron forms a  $H_2$ -type ellipsoidal MO with one of the  $C$ -atom electrons. However, such a bond is not possible with the outer  $C$  electrons in their ground state since the resulting  $H_2$ -type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon  $2p$  shell, which is not energetically stable. Thus, when bonding the carbon  $2s$  and  $2p$  shells hybridize to form a single  $2sp^3$  shell as an energy minimum.

15

The  $C$  electron configuration given in the Six-Electron Atoms section is  $1s^2 2s^2 2p^2$ , and the orbital arrangement is

$$\begin{array}{ccc} & \text{2p state} & \\ \uparrow & \uparrow & \text{---} \\ \hline 1 & 0 & -1 \end{array} \quad (13.419)$$

corresponding to the ground state  $^3P_0$ . The radius  $r_6$  of the  $2p$  shell given by Eq. (10.122) is

$$r_6 = 1.20654a_0 \quad (13.420)$$

The energy of the carbon  $2p$  shell is the negative of the ionization energy of the carbon atom given by Eq. (10.123). Experimentally, the energy is [12]

$$E(C, 2p \text{ shell}) = -E(\text{ionization}; C) = -11.2603 \text{ eV} \quad (13.421)$$

The  $C2s$  atomic orbital (AO) combines with the  $C2p$  AOs to form a single  $2sp^3$  hybridized orbital (HO) with the orbital arrangement

25

$$\begin{array}{cccc}
 & & 179 & \\
 & & 2sp^3 \text{ state} & \\
 \uparrow & \uparrow & \uparrow & \uparrow \\
 0,0 & 1,-1 & 1,0 & 1,1
 \end{array} \quad (13.422)$$

where the quantum numbers  $(\ell, m_\ell)$  are below each electron. The total energy of the state is given by the sum over the four electrons. The sum  $E_T(C, 2sp^3)$  of calculated energies of  $C$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$E_T(C, 2sp^3) = 64.3921 \text{ eV} + 48.3125 \text{ eV} + 24.2762 \text{ eV} + 11.27671 \text{ eV} = 148.25751 \text{ eV} \quad (13.423)$$

which agrees well with the sum of  $148.02532 \text{ eV}$  from the experimental [6] values. The orbital-angular-momentum interactions cancel such that the energy of the  $E_T(C, 2sp^3)$  is purely Coulombic. By considering that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{2sp^3}$  of the  $C2sp^3$  shell may be calculated from the Coulombic energy using Eq. (10.102):

$$r_{2sp^3} = \sum_{n=2}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0 (e148.25751 \text{ eV})} = \frac{10e^2}{8\pi\epsilon_0 (e148.25751 \text{ eV})} = 0.91771a_0 \quad (13.424)$$

Using Eqs. (10.102) and (13.424), the Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E_{Coulomb}(C, 2sp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{2sp^3}} = \frac{-e^2}{8\pi\epsilon_0 0.91771a_0} = -14.82575 \text{ eV} \quad (13.425)$$

During hybridization, one of the spin-paired  $2s$  electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152) at the initial radius of the  $2s$  electrons. From Eq. (10.62) with  $Z = 6$ , the radius  $r_3$  of  $C2s$  shell is

$$r_3 = 0.84317a_0 \quad (13.426)$$

Using Eqs. (13.152) and (13.426), the unpairing energy is

$$E(\text{magnetic}) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} = \frac{8\pi\mu_0 \mu_B^2}{(0.84317a_0)^3} = 0.19086 \text{ eV} \quad (13.427)$$

Using Eqs. (13.425) and (13.427), the energy  $E(C, 2sp^3)$  of the outer electron of the  $C2sp^3$

shell is

$$\begin{aligned}
 E(C, 2sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{2sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} \\
 &= -14.82575 \text{ eV} + 0.19086 \text{ eV} \\
 &= -14.63489 \text{ eV}
 \end{aligned}
 \tag{13.428}$$

The nitrogen atom's  $2p$ -shell electron configuration given by Eq. (10.134) is the same as that of the  $C2sp^3$  shell, and nitrogen's calculated energy of  $14.61664 \text{ eV}$  given by Eq. (10.143) is a close match with  $E(C, 2sp^3)$ . Thus, the binding should be very similar except that four bonds to hydrogen can occur with carbon.

The carbon  $C2sp^3$  electron combines with the  $H1s$  electron to form a molecular orbital. The proton of the  $H$  atom and the nucleus of the  $C$  atom are along the internuclear axis and serve as the foci. Due to symmetry, the other  $C$  electrons are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix IV.) Thus, the energies in the  $CH$  MO involve only the  $C2sp^3$  and  $H1s$  electrons. The forces are determined by these energies.

As in the case of  $H_2$ , the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell. Thus, the MO surface comprises a prolate spheroid at the  $H$  proton that is continuous with the  $C2sp^3$  shell at the  $C$  atom whose nucleus serves as the other focus. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the  $C2sp^3$  shell. As in the case with  $OH$  and  $NH$ , the linear combination of the  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  HO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the  $C2sp^3$  HO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $CH$  MO must comprise 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO:

$$1 \text{ } C2sp^3 + 0.75 \text{ } H_2 \text{ MO} \rightarrow CH \text{ MO} \tag{13.429}$$

The force balance of the  $CH$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.429) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

As in the case with  $OH$  (Eq. (13.57)), the  $H_2$ -type ellipsoidal MO comprises 75% of the  $CH$  MO; so, the electron charge density in Eq. (11.65) is given by  $-0.75e$ . The force constant  $k'$  to determine the ellipsoidal parameter  $c'$  in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin to each focus  $c'$  is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal  $C-H$ -bond MO  $b=c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of the  $CH$  MO. Since the  $CH$  MO comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $C2sp^3$  HO, the energy  $E(C, 2sp^3)$  in Eq. (13.428) adds to that of the  $H_2$ -type ellipsoidal MO to give the total energy of the  $CH$  MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ ,  $T$ , and  $V_m$  are those of  $H_2$  (Eqs. (11.207-11.212)) except that they are corrected for electron hybridization. Hybridization gives rise to the  $C2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  given by Eq. (13.425). To meet the equipotential condition of the union of the  $H_2$ -type-ellipsoidal-MO and the  $C2sp^3$  HO, the electron energies are normalized by the ratio of  $14.82575 eV$ , the magnitude of  $E_{Coulomb}(C, 2sp^3)$  given by Eq. (13.425), and  $13.605804 eV$ , the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). This normalizes the energies to match that of the Coulombic energy alone to meet the energy matching condition of the  $CH$  MO under the influence of the proton and the  $C$  nucleus. The hybridization energy factor  $C_{C2sp^3HO}$  is

$$C_{C2sp^3HO} = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{2sp^3}}} = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 0.91771a_0}} = \frac{13.605804 eV}{14.82575 eV} = 0.91771 \quad (13.430)$$

The total energy  $E_T(CH)$  of the  $CH$  MO is given by the sum of the energies of the orbitals, the  $H_2$ -type ellipsoidal MO and the  $C2sp^3$  HO, that form the hybridized  $CH$  MO.  $E_T(CH)$  follows from by Eq. (13.74) for  $OH$ , but the energy of the  $C2sp^3$  HO given by Eq. (13.428) is substituted for the energy of  $O$  and the  $H_2$ -type-ellipsoidal-MO energies are

those of  $H_2$  (Eqs. (11.207-11.212)) multiplied by the electron hybridization factor rather than by the factor of 0.75:

$$E_T(CH) = E_T + E(C, 2sp^3) = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} \quad (13.431)$$

To match the boundary condition that the total energy of the entire the  $H_2$ -type ellipsoidal MO is given by Eqs. (11.212) and (13.75),  $E_T(CH)$  given by Eq. (13.431) is set equal to Eq. (13.75):

$$E_T(CH) = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} = -31.63536831 \text{ eV} \quad (13.432)$$

From the energy relationship given by Eq. (13.432) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.432) gives

$$\frac{e^2}{8\pi\epsilon_0 \sqrt{\frac{2aa_0}{3}}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right] = e17.00048 \quad (13.433)$$

The most convenient way to solve Eq. (13.433) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.67465a_0 = 8.86186 \times 10^{-11} \text{ m} \quad (13.434)$$

Substitution of Eq. (13.434) into Eq. (13.60) gives

$$c' = 1.05661a_0 = 5.59136 \times 10^{-11} \text{ m} \quad (13.435)$$

The internuclear distance given by multiplying Eq. (13.435) by two is

$$2c' = 2.11323a_0 = 1.11827 \times 10^{-10} \text{ m} \quad (13.436)$$

The experimental bond distance is [14]

$$2c' = 1.1198 \times 10^{-10} \text{ m} \quad (13.437)$$

Substitution of Eqs. (13.434-13.435) into Eq. (13.62) gives

$$b = c = 1.29924a_0 = 6.87527 \times 10^{-11} \text{ m} \quad (13.438)$$

Substitution of Eqs. (13.434-13.435) into Eq. (13.63) gives

$$e = 0.63095 \quad (13.439)$$

The nucleus of the  $H$  atom and the nucleus of the  $C$  atom comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{2sp^3} = 0.91771a_0$  is the radius of the

5  $C2sp^3$  shell. Substitution of Eqs. (13.434-13.435) into Eq. (13.261) gives

$$\theta' = 81.03^\circ \quad (13.440)$$

Then, the angle  $\theta_{C2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C2sp^3HO} = 180^\circ - 81.03^\circ = 98.97^\circ \quad (13.441)$$

10 as shown in Figure 14.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C2sp^3$

15 radial vector obeys the following relationship:

$$r_{2sp^3} \sin \theta_{C2sp^3HO} = 0.91771a_0 \sin \theta_{C2sp^3HO} = b \sin \theta_{H_2MO} \quad (13.442)$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{0.91771a_0 \sin \theta_{C2sp^3HO}}{b} = \sin^{-1} \frac{0.91771a_0 \sin 98.97^\circ}{b} \quad (13.443)$$

with the use of Eq. (13.441). Substitution of Eq. (13.438) into Eq. (13.443) gives

$$20 \quad \theta_{H_2MO} = 44.24^\circ \quad (13.444)$$

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a \cos \theta_{H_2MO} \quad (13.445)$$

Substitution of Eqs. (13.434) and (13.444) into Eq. (13.445) gives

$$25 \quad d_{H_2MO} = 1.19968a_0 = 6.34845 \times 10^{-11} \text{ m} \quad (13.446)$$

The distance  $d_{C2sp^3HO}$  along the internuclear axis from the origin of the  $C$  atom to the point of intersection of the orbitals is given by

$$d_{C2sp^3HO} = d_{H_2MO} - c' \quad (13.447)$$

Substitution of Eqs. (13.435) and (13.446) into Eq. (13.447) gives

$$d_{C2sp^3HO} = 0.14307a_0 = 7.57090 \times 10^{-12} \text{ m} \quad (13.448)$$

As shown in Eq. (13.429), the uniform charge-density in the  $C2sp^3$  HO is increased by a factor of 0.25 and the  $H$ -atom density is decreased by a factor of 0.25. Using the orbital composition of  $CH$  (Eq. (13.429)), the radii of  $C1s = 0.17113a_0$  (Eq. (10.51)) and

- 5  $C2sp^3 = 0.91771a_0$  (Eq. (10.424)) shells, and the parameters of the  $CH$  MO given by Eqs. (13.3-13.4), (13.434-13.436), and (13.438-13.448), the dimensional diagram and charge-density of the  $CH$  MO comprising the linear combination of the  $H_2$ -type ellipsoidal MO and the  $C2sp^3$  HO according to Eq. (13.429) are shown in Figures 14 and 15, respectively.

10

### ENERGIES OF $CH$

The energies of  $CH$  are given by the substitution of the semiprincipal axes (Eqs. (13.434-13.435) and (13.438)) into the energy equations, (Eq. (13.431) and Eqs. (11.207-11.211)) that are corrected for electron hybridization using Eq. (13.430):

$$15 \quad V_e = (0.91771) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -35.12015 \text{ eV} \quad (13.449)$$

$$V_p = \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 12.87680 \text{ eV} \quad (13.450)$$

$$T = (0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 10.48582 \text{ eV} \quad (13.451)$$

$$V_m = (0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -5.24291 \text{ eV} \quad (13.452)$$

$$E_T(CH) = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} = -31.63533 \text{ eV} \quad (13.453)$$

20

where  $E_T(CH)$  is given by Eq. (13.431) which is reiteratively matched to Eq. (13.75) within five-significant-figure round-off error.



VIBRATION AND ROTATION OF  $CH$ 

The vibrational energy of  $CH$  may be solved in the same manner as that of  $OH$  and  $NH$  except that the force between the electrons and the foci given by Eq. (13.102) is doubled due to electron hybridization of the two shells of carbon after Eq. (11.141). From Eqs. (13.102-5 13.106) with the substitution of the  $CH$  parameters, the angular frequency of the oscillation is

$$\begin{aligned}\omega &= \sqrt{\frac{\frac{0.75e^2}{4\pi\epsilon_0 b^3} - \frac{e^2}{8\pi\epsilon_0 (2c')^3}}{\mu}} \\ &= \sqrt{\frac{\frac{0.75e^2}{4\pi\epsilon_0 (1.29924a_0)^3} - \frac{e^2}{8\pi\epsilon_0 (2.11323a_0)^3}}{\frac{12}{13}m_p}} \\ &= 5.39828 \times 10^{14} \text{ rad/s}\end{aligned}\quad (13.454)$$

where  $b$  is given by Eq. (13.438),  $2c'$  is given by Eq. (13.436), and the reduced mass of  $^{12}CH$  is given by:

$$10 \quad \mu_{^{12}CH} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1)(12)}{1+12} m_p \quad (13.455)$$

where  $m_p$  is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency,  $\omega(0)$ , for  $^{12}CH$  given by Eqs. (11.136), (11.148), and (13.454) is

$$15 \quad \omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{449.94 \text{ Nm}^{-1}}{\mu}} = 5.39828 \times 10^{14} \text{ radians/s} \quad (13.456)$$

where the reduced nuclear mass of  $^{12}CH$  is given by Eq.(13.455) and the spring constant,  $k(0)$ , given by Eqs. (11.136) and (13.454) is

$$k(0) = 449.94 \text{ Nm}^{-1} \quad (13.457)$$

The  $^{12}CH$  transition-state vibrational energy,  $E_{vib}(0)$ , given by Planck's equation (Eq. 20 (11.127)) is:

$$E_{vib}(0) = \hbar\omega = \hbar 5.39828 \times 10^{14} \text{ rad/s} = 0.35532 \text{ eV} = 2865.86 \text{ cm}^{-1} \quad (13.458)$$

$\omega_e$ , from the experimental curve fit of the vibrational energies of  $^{12}CH$  is [14]

$$\omega_e = 2861.6 \text{ cm}^{-1} \quad (13.459)$$

Using Eqs. (13.112-13.118) with  $E_{vib}(0)$  given by Eq. (13.458) and  $D_0$  given by Eq. (13.488), the  $^{12}\text{CH}$   $\nu = 1 \rightarrow \nu = 0$  vibrational energy,  $E_{vib}(1)$  is

$$E_{vib}(1) = 0.33879 \text{ eV} \quad (2732.61 \text{ cm}^{-1}) \quad (13.460)$$

- 5 The experimental vibrational energy of  $^{12}\text{CH}$  using  $\omega_e$  and  $\omega_e x_e$  [14] according to K&P [15] is

$$E_{vib}(1) = 0.33885 \text{ eV} \quad (2733 \text{ cm}^{-1}) \quad (13.461)$$

Using Eq. (13.113) with  $E_{vib}(1)$  given by Eq. (13.460) and  $D_0$  given by Eq. (13.488), the anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{12}\text{CH}$  is

$$10 \quad \omega_0 x_0 = 66.624 \text{ cm}^{-1} \quad (13.462)$$

The experimental anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{12}\text{CH}$  [14] is

$$\omega_0 x_0 = 64.3 \text{ cm}^{-1} \quad (13.463)$$

The vibrational energies of successive states are given by Eqs. (13.458), (13.112), and (13.462).

- 15 Using  $b$  given by Eq. (13.438),  $2c'$  given by Eq. (13.436),  $D_0$  given by Eq. (13.490), and the reduced nuclear mass of  $^{12}\text{CD}$  given by

$$\mu_{^{12}\text{CD}} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(2)(12)}{2+12} m_p \quad (13.464)$$

where  $m_p$  is the proton mass, the corresponding parameters for deuterium carbide  $^{12}\text{CD}$  (Eqs. (13.102-13.121)) are

$$20 \quad \omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{449.94 \text{ Nm}^{-1}}{\mu}} = 3.96126 \times 10^{14} \text{ radians/s} \quad (13.465)$$

$$k(0) = 449.94 \text{ Nm}^{-1} \quad (13.466)$$

$$E_{vib}(0) = \hbar\omega = \hbar 3.96126 \times 10^{14} \text{ rad/s} = 0.26074 \text{ eV} = 2102.97 \text{ cm}^{-1} \quad (13.467)$$

$$E_{vib}(1) = 0.25173 \text{ eV} \quad (2030.30 \text{ cm}^{-1}) \quad (13.468)$$

$$\omega_0 x_0 = 36.335 \text{ cm}^{-1} \quad (13.469)$$

- 25  $\omega_e$ , from the experimental curve fit of the vibrational energies of  $^{12}\text{CD}$  is [14]

$$\omega_e = 2101.0 \text{ cm}^{-1} \quad (13.470)$$

The experimental vibrational energy of  $^{12}\text{CD}$  using  $\omega_e$  and  $\omega_e x_e$  [14] according to K&P [15] is

$$E_{vib}(1) = 0.25189 \text{ eV} \quad (2031.6 \text{ cm}^{-1}) \quad (13.471)$$

and the experimental anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{12}\text{CD}$  is [14]

$$5 \quad \omega_0 x_0 = 34.7 \text{ cm}^{-1} \quad (13.472)$$

which match the predictions given by Eqs. (13.467), (13.468) and (13.469), respectively.

Using Eqs. (13.133-13.134) and the internuclear distance,  $r = 2c'$ , and reduced mass of  $^{12}\text{CH}$  given by Eqs. (13.436) and (13.455), respectively, the corresponding  $B_e$  is

$$B_e = 14.498 \text{ cm}^{-1} \quad (13.473)$$

10 The experimental  $B_e$  rotational parameter of  $^{12}\text{CH}$  is [14]

$$B_e = 14.457 \text{ cm}^{-1} \quad (13.474)$$

Using the internuclear distance,  $r = 2c'$ , and reduced mass of  $^{12}\text{CD}$  given by Eqs. (13.436) and (13.464), respectively, the corresponding  $B_e$  is

$$B_e = 7.807 \text{ cm}^{-1} \quad (13.475)$$

15 The experimental  $B_e$  rotational parameter of  $^{12}\text{CD}$  is [14]

$$B_e = 7.808 \text{ cm}^{-1} \quad (13.476)$$

### THE DOPPLER ENERGY TERMS OF $^{12}\text{CH}$ AND $^{12}\text{CD}$

The equations of the radiation reaction force of hydrogen and deuterium carbide are the same as those of the corresponding hydroxyl and hydrogen nitride radicals with the substitution of the hydrogen and deuterium carbide parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 2.41759 \times 10^{16} \text{ rad/s} \quad (13.477)$$

where  $b$  is given by Eq. (13.438). The kinetic energy,  $E_K$ , is given by Planck's equation

25 (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.41759 \times 10^{16} \text{ rad/s} = 15.91299 \text{ eV} \quad (13.478)$$

In Eq. (11.181), substitution of the total energy of  $CH$ ,  $E_T(CH)$ , (Eq. (13.432)) for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.478) for  $\bar{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(15.91299 \text{ eV})}{m_e c^2}} = -0.24966 \text{ eV} \quad (13.479)$$

5 In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $CH$  due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (13.479) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational  
10 energy of  $CH$ . The experimental  $^{12}CH$   $\omega_e$  is  $2861.6 \text{ cm}^{-1}$  ( $0.35480 \text{ eV}$ ) [14] which matches the predicted  $\omega_e$  of  $2865.86 \text{ cm}^{-1}$  ( $0.35532 \text{ eV}$ ) given by Eq. (13.458). Using the predicted  $\omega_e$  for  $\bar{E}_{Kvib}$  of the transition state,  $\bar{E}_{osc}(^{12}CH)$  is

$$\bar{E}_{osc}(^{12}CH) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.480)$$

$$\bar{E}_{osc}(^{12}CH) = -0.24966 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) = -0.07200 \text{ eV} \quad (13.481)$$

15 The experimental  $^{12}CD$   $\omega_e$  is  $2101.0 \text{ cm}^{-1}$  ( $0.26049 \text{ eV}$ ) [14] which matches the predicted  $\omega_e$  of  $2102.97 \text{ cm}^{-1}$  ( $0.26074 \text{ eV}$ ) given by Eq. (13.467). Using Eq. (13.479) and the predicted  $\omega_e$  for  $\bar{E}_{Kvib}$  of the transition state,  $\bar{E}_{osc}(^{12}CD)$  is

$$\bar{E}_{osc}(^{12}CD) = -0.24966 \text{ eV} + \frac{1}{2} (0.26074 \text{ eV}) = -0.11929 \text{ eV} \quad (13.482)$$

## 20 TOTAL AND BOND ENERGIES OF $^{12}CH$ AND $^{12}CD$

$E_{T+osc}(^{12}CH)$ , the total energy of the  $^{12}CH$  radical including the Doppler term, is given by the sum of  $E_T(CH)$  (Eq. (13.432)) and  $\bar{E}_{osc}(^{12}CH)$  given by Eq. (13.481):

$$\begin{aligned} E_{T+osc}(^{12}CH) &= V_e + T + V_m + V_p + E(C, 2sp^3) + \bar{E}_{osc}(^{12}CH) \\ &= E_T(CH) + \bar{E}_{osc}(^{12}CH) \end{aligned} \quad (13.483)$$

$$E_{T+osc}({}^{12}\text{CH}) = \left\{ \left( \frac{-e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} \right) \right. \\ \left. \left( 1 + \sqrt{\frac{2\hbar \sqrt{\frac{3}{4} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2}} \right) + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right\} \\ = -31.63537 \text{ eV} - 0.24966 \text{ eV} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}$$

(13.484)

From Eqs. (13.480-13.481) and (13.483-13.484), the total energy of  ${}^{12}\text{CH}$  is

$$E_{T+osc}({}^{12}\text{CH}) = -31.63537 \text{ eV} + \bar{E}_{osc}({}^{12}\text{CH}) \\ = -31.63537 \text{ eV} - 0.24966 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) \\ = -31.70737 \text{ eV} \quad (13.485)$$

5 where the predicted  $\omega_e$  (Eq. (13.458)) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.  $E_{T+osc}({}^{12}\text{CD})$ , the total energy of  ${}^{12}\text{CD}$  including the Doppler term, is given by the sum of  $E_T(\text{CD}) = E_T(\text{CH})$  (Eq. (13.432)) and  $\bar{E}_{osc}({}^{12}\text{CD})$  given by Eq. (13.482):

$$E_{T+osc}({}^{12}\text{CD}) = -31.63537 \text{ eV} + \bar{E}_{osc}({}^{12}\text{CD}) \\ = -31.63537 \text{ eV} - 0.24966 \text{ eV} + \frac{1}{2} (0.26074 \text{ eV}) \\ = -31.75462 \text{ eV} \quad (13.486)$$

where the predicted  $\omega_e$  (Eq. (13.467)) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

10 The  $\text{CH}$  bond dissociation energy,  $E_D({}^{12}\text{CH})$ , is given by the sum of the total energies of the  $\text{C}2sp^3$  HO and the hydrogen atom minus  $E_{T+osc}({}^{12}\text{CH})$ <sup>3</sup>:

$$E_D({}^{12}\text{CH}) = E(\text{C}, 2sp^3) + E(\text{H}) - E_{T+osc}({}^{12}\text{CH}) \quad (13.487)$$

<sup>3</sup> The hybridization energy is the difference between  $E(\text{C}, 2sp^3)$  given by Eq. (13.428) and  $E(\text{C}, 2p \text{ shell})$  given by Eq. (13.421). Since this term adds to  $E(\text{C}, 2p \text{ shell})$  to give the total energy from which  $E_{T+osc}({}^{12}\text{CH})$  is subtracted to give  $E_D({}^{12}\text{CH})$ , it is more convenient to simply use  $E(\text{C}, 2sp^3)$  directly in Eq. (13.487).

$E(C, 2sp^3)$  is given by Eq. (13.428), and  $E_D(H)$  is given by Eq. (13.154). Thus, the  $^{12}CH$  bond dissociation energy,  $E_D(^{12}CH)$ , given by Eqs. (13.154), (13.428), (13.485), and (13.487) is

$$\begin{aligned} E_D(^{12}CH) &= -(14.63489 \text{ eV} + 13.59844 \text{ eV}) - E_{T+osc}(CH) \\ &= -28.23333 \text{ eV} - (-31.70737 \text{ eV}) \\ &= 3.47404 \text{ eV} \end{aligned} \quad (13.488)$$

5 The experimental  $^{12}CH$  bond dissociation energy is [14]

$$E_D(^{12}CH) = 3.47 \text{ eV} \quad (13.489)$$

which is a close match to that of  $NH$  as predicted based on the match between the  $N$  and  $C2sp^3$  HO energies and electron configurations.

The  $^{12}CD$  bond dissociation energy,  $E_D(^{12}CD)$ , is given by the sum of the total  
10 energies of the  $C2sp^3$  HO and the deuterium atom minus  $E_{T+osc}(CD)$ :

$$E_D(^{12}CD) = E(C, 2sp^3) + E(D) - E_{T+osc}(^{12}CD) \quad (13.490)$$

$E(C, 2sp^3)$  is given by Eq. (13.428), and  $E_D(D)$  is given by Eq. (13.155). Thus, the  $^{12}CD$  bond dissociation energy,  $E_D(^{12}CD)$ , given by Eqs. (13.155), (13.428), (13.486), and (13.490) is

$$\begin{aligned} E_D(^{12}CD) &= -(14.63489 \text{ eV} + 13.603 \text{ eV}) - E_{T+osc}(^{12}CD) \\ 15 \quad &= -28.23789 \text{ eV} - (-31.75462 \text{ eV}) \\ &= 3.51673 \text{ eV} \end{aligned} \quad (13.491)$$

The experimental  $^{12}CD$  bond dissociation energy is [14]

$$E_D(^{12}CD) = 3.52 \text{ eV} \quad (13.492)$$

The results of the determination of bond parameters of  $CH$  and  $CD$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form,  
20 exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## DIHYDROGEN CARBIDE ( $CH_2$ )

The dihydrogen carbide radical  $CH_2$  is formed by the reaction of a hydrogen atom with a  
25 hydrogen carbide radical:



$CH_2$  can be solved using the same principles as those used to solve  $H_2O$  and  $NH_2$  with the exception that the carbon  $2s$  and  $2p$  shells hybridize to form a single  $2sp^3$  shell as an energy minimum. Two diatomic molecular orbitals (MOs) developed in the Nature of the  
 5 Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with two carbon  $2sp^3$  hybridized orbitals (HOs) to form the MO of  $CH_2$ . The solution is very similar to that of  $CH$  except that there are two  $CH$  bonds in  $CH_2$ .

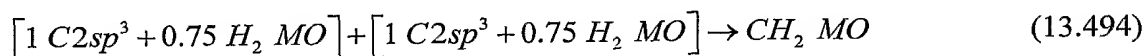
## 10 FORCE BALANCE OF $CH_2$

$CH_2$  comprises two chemical bonds between carbon and hydrogen atoms. Each  $C-H$  bond comprises two spin-paired electrons with one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom. Each  $H$ -atom electron forms a  $H_2$ -type ellipsoidal MO with an unpaired  $C$ -atom electrons. However, such a bond is not  
 15 possible with the outer two  $C$  electrons in their ground state since the resulting  $H_2$ -type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon  $2p$  shell, which is not energetically stable. Thus, when bonding the carbon  $2s$  and  $2p$  shells hybridize to form a single  $2sp^3$  shell as an energy minimum. The electron configuration and the energy,  $E(C, 2sp^3)$ , of the  $C2sp^3$  shell is given by Eqs. (13.422), and (13.428),  
 20 respectively.

For each  $C-H$  bond, a  $C2sp^3$  electron combines with the  $H1s$  electron to form a molecular orbital. The proton of the  $H$  atom and the nucleus of the  $C$  atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , each of the two  $C-H$ -bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend  
 25 into the  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the  $H$  proton that is continuous with the  $C2sp^3$  shell at the  $C$  atom whose nucleus serves as the other focus. The radius and the energy of the  $C2sp^3$  shell are unchanged with bond formation. The central paramagnetic force due to spin of each  $C-H$  bond is provided by

the spin-pairing force of the  $CH_2$  MO that has the symmetry of an  $s$  orbital that superimposes with the  $C2sp^3$  orbitals such that the corresponding angular momenta are unchanged.

The energies in the  $CH_2$  MO involve only each  $C2sp^3$  and each  $H1s$  electron with the formation of each  $C-H$  bond. The sum of the energies of the  $H_2$ -type ellipsoidal MOs is matched to that of the  $C2sp^3$  shell. As in the cases with of  $OH$ ,  $H_2O$ ,  $NH$ ,  $NH_2$ ,  $NH_3$ , and  $CH$  the linear combination of each  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  HO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the  $C2sp^3$  HO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $CH_2$  MO must comprise two  $C-H$  bonds with each comprising 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO:



The force balance of the  $CH_2$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.494) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant  $k'$  to determine the ellipsoidal parameter  $c'$  of the each  $H_2$ -type-ellipsoidal-MO component of the  $CH_2$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each  $C-H$ -bond MO to each focus  $c'$  is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal  $C-H$ -bond MO  $b = c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of each  $C-H$ -bond MO. Since each of the two prolate spheroidal  $C-H$ -bond MOs comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $C2sp^3$  HO, the energy  $E(C, 2sp^3)$  in Eq. (13.428) adds to that of the two corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $CH_2$  MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH_2$  MO are solved.



The energy components of  $V_e$ ,  $V_p$ ,  $T$ , and  $V_m$  are twice those of  $CH$  corresponding to the two  $C-H$  bonds. Since the each prolate spheroidal  $H_2$ -type MO transitions to the  $C2sp^3$  HO and the energy of the  $C2sp^3$  shell must remain constant and equal to the  $E(C, 2sp^3)$  given by Eq. (13.428), the total energy  $E_T(CH_2)$  of the  $CH_2$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C2sp^3$  HO and the two  $H_2$ -type ellipsoidal MOs that forms the  $CH_2$  MO as given by Eq. (13.494). Using Eq. (13.431),  $E_T(CH_2)$  is given by

$$\begin{aligned} E_T(CH_2) &= E_T + E(C, 2sp^3) \\ &= -\frac{e^2}{4\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} \end{aligned} \quad (13.495)$$

The two hydrogen atoms and the hybridized carbon atom can achieve an energy minimum as a linear combination of two  $H_2$ -type ellipsoidal MOs each having the proton and the carbon nucleus as the foci. Hybridization gives rise to the  $C2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  given by Eq. (13.425). To meet the equipotential condition of the union of the  $H_2$ -type-ellipsoidal-MO and the  $C2sp^3$  HO, the electron energies in Eq. (13.495) were normalized by the ratio of 14.82575 eV, the magnitude of  $E_{Coulomb}(C, 2sp^3)$  given by Eq. (13.425), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). The factor given by Eq. (13.430) normalized the energies to match that of the Coulombic energy alone to meet the energy matching condition of each  $C-H$ -bond MO under the influence of the proton and the  $C$  nucleus. Each  $C-H$ -bond MO comprises the same  $C2sp^3$  shell having its energy normalized to that of the Coulombic energy between the electron and a charge of  $+e$  at the carbon focus of the  $CH_2$  MO. Thus, the energy of the  $CH_2$  MO is also given by the sum of that of the two  $H_2$ -type ellipsoidal MOs given by Eq. (11.212) minus the Coulombic energy,  $E_{Coulomb}(H) = -13.605804 \text{ eV}$ , of the redundant  $+e$  of the linear combination:

$$\begin{aligned} E_T(2H_2 - H) &= -\frac{e^2}{4\pi\epsilon_0 a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] - E_{Coulomb}(H) \\ &= 2(-31.63536831 \text{ eV}) - (-13.605804 \text{ eV}) \\ &= -49.66493 \text{ eV} \end{aligned} \quad (13.496)$$

$E_T(CH_2)$  given by Eq. (13.495) is set equal to two times the energy of the  $H_2$ -type ellipsoidal MO minus the Coulombic energy of  $H$  given by Eq. (13.496):

$$E_T(CH_2) = -\frac{e^2}{4\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} = -49.66493 \text{ eV} \quad (13.497)$$

- 5 From the energy relationship given by Eq. (13.497) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH_2$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.497) gives

$$\frac{e^2}{4\pi\epsilon_0 \sqrt{\frac{2aa_0}{3}}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right] = e35.03004 \quad (13.498)$$

- The most convenient way to solve Eq. (13.498) is by the reiterative technique using a  
10 computer. The result to within the round-off error with five-significant figures is

$$a = 1.64010a_0 = 8.67903 \times 10^{-11} \text{ m} \quad (13.499)$$

Substitution of Eq. (13.499) into Eq. (13.60) gives

$$c' = 1.04566a_0 = 5.53338 \times 10^{-11} \text{ m} \quad (13.500)$$

The internuclear distance given by multiplying Eq. (13.500) by two is

$$15 \quad 2c' = 2.09132a_0 = 1.10668 \times 10^{-10} \text{ m} \quad (13.501)$$

The experimental bond distance is [38]

$$2c' = 1.111 \times 10^{-10} \text{ m} \quad (13.502)$$

Substitution of Eqs. (13.499-13.500) into Eq. (13.62) gives

$$b = c = 1.26354a_0 = 6.68635 \times 10^{-11} \text{ m} \quad (13.503)$$

- 20 Substitution of Eqs. (13.499-13.500) into Eq. (13.63) gives

$$e = 0.63756 \quad (13.504)$$

- The nucleus of the  $H$  atom and the nucleus of the  $C$  atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of each  $H_2$ -type ellipsoidal MO and the  $C2sp^3$  HO are given by Eqs. (13.84-13.95), (13.261-13.270), and (13.440-  
25 13.448). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{2sp^3} = 0.91771a_0$  is the radius of the  $C2sp^3$  shell. Substitution of Eqs. (13.499-13.500) into Eq. (13.261) gives

$$\theta' = 84.54^\circ \quad (13.505)$$

Then, the angle  $\theta_{C2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C2sp^3HO} = 180^\circ - 84.54^\circ = 95.46^\circ \quad (13.506)$$

5 as shown in Figure 14. The angle  $\theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  radial vector given by Eqs. (13.442-13.443), (13.503), and (13.506) is

$$\theta_{H_2MO} = 46.30^\circ \quad (13.507)$$

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.445), (13.499), and (13.507) is

$$d_{H_2MO} = 1.13305a_0 = 5.99585 \times 10^{-11} \text{ m} \quad (13.508)$$

The distance  $d_{C2sp^3HO}$  along the internuclear axis from the origin of the  $C$  atom to the point of intersection of the orbitals given by Eqs. (13.447), (13.500), and (13.508) is

$$15 \quad d_{C2sp^3HO} = 0.08739a_0 = 4.62472 \times 10^{-12} \text{ m} \quad (13.509)$$

As shown in Eq. (13.494), the uniform charge-density in the  $C2sp^3$  HO is increased by a factor of 0.25 and the  $H$ -atom density is decreased by a factor of 0.25 for by each  $C-H$  bond. Using the orbital composition of  $CH_2$  (Eq. (13.494)), the radii of  $C1s = 0.17113a_0$  (Eq. (10.51)) and  $C2sp^3 = 0.91771a_0$  (Eq. (10.424)) shells, and the parameters of the  $CH_2$  MO given by Eqs. (13.3-13.4), (13.499-13.501), and (13.503-13.509), the charge-density of the  $CH_2$  MO comprising the linear combination of two  $C-H$ -bond MOs is shown in Figure 16. Each  $C-H$ -bond MO comprises a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO having the dimensional diagram shown in Figure 14.

## 25 ENERGIES OF $CH_2$

The energies of  $CH_2$  are two times those of  $CH$  and are given by the substitution of the semiprincipal axes (Eqs. (13.499-13.500) and (13.503)) into the energy equations Eq. (13.495) and (Eqs. (13.449-13.452)) that are multiplied by two:

$$V_e = (0.91771) \frac{-2e^2}{4\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -72.03287 \text{ eV} \quad (13.510)$$

$$V_p = \frac{e^2}{4\pi\epsilon_0\sqrt{a^2-b^2}} = 26.02344 \text{ eV} \quad (13.511)$$

$$T = (0.91771) \frac{\hbar^2}{m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 21.95990 \text{ eV} \quad (13.512)$$

$$V_m = (0.91771) \frac{-\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -10.97995 \text{ eV} \quad (13.513)$$

$$5 \quad E_T(CH_2) = -\frac{e^2}{4\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} = -49.66437 \text{ eV} \quad (13.514)$$

where  $E_T(CH_2)$  is given by Eq. (13.495) which is reiteratively matched to Eq. (13.496) within five-significant-figure round-off error.

## 10 VIBRATION OF $CH_2$

The vibrational energy levels of  $CH_2$  may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of  
15 Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF $^{12}CH_2$

The reentrant oscillation of hybridized orbitals in the transition state is not coupled. Therefore, the equations of the radiation reaction force of dihydrogen and dideuterium  
20 carbide are the same as those of the corresponding hydrogen carbide radicals with the substitution of the dihydrogen and dideuterium carbide parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 2.52077 \times 10^{16} \text{ rad/s} \quad (13.515)$$

where  $b$  is given by Eq. (13.503). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.52077 \times 10^{16} \text{ rad/s} = 16.59214 \text{ eV} \quad (13.516)$$

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.516) for  $\bar{E}_K$  gives the Doppler energy of the electrons of each of the two bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(16.59214 \text{ eV})}{m_e c^2}} = -0.25493 \text{ eV} \quad (13.517)$$

10 In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $CH_2$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (13.517) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which  
15 is 1/2 of the vibrational energy of each  $C-H$  bond. Using  $\omega_e$  given by Eq. (13.458) for  $\bar{E}_{Kvib}$  of the transition state having two independent bonds,  $\bar{E}'_{osc}({}^{12}CH_2)$  per bond is

$$\bar{E}'_{osc}({}^{12}CH_2) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.518)$$

$$\bar{E}'_{osc}({}^{12}CH_2) = -0.25493 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) = -0.07727 \text{ eV} \quad (13.519)$$

Given that the vibration and reentrant oscillation is for two  $C-H$  bonds,  $\bar{E}_{osc}({}^{12}CH_2)$ , is:

$$\begin{aligned} \bar{E}_{osc}({}^{12}CH_2) &= 2 \left( \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \\ &= 2 \left( -0.25493 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) \right) \\ &= -0.15454 \text{ eV} \end{aligned} \quad (13.520)$$

TOTAL AND BOND ENERGIES OF  $^{12}\text{CH}_2$ 

$E_{T+osc}(^{12}\text{CH}_2)$ , the total energy of the  $^{12}\text{CH}_2$  radical including the Doppler term, is given by the sum of  $E_T(\text{CH}_2)$  (Eq. (13.497)) and  $\bar{E}_{osc}(^{12}\text{CH}_2)$  given by Eq. (13.520):

$$\begin{aligned} E_{T+osc}(\text{CH}_2) &= V_e + T + V_m + V_p + E(C, 2sp^3) + \bar{E}_{osc}(^{12}\text{CH}_2) \\ &= E_T(\text{CH}_2) + \bar{E}_{osc}(^{12}\text{CH}_2) \end{aligned} \quad (13.521)$$

$$\begin{aligned} E_{T+osc}(^{12}\text{CH}_2) &= \left\{ \left( \frac{-e^2}{4\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} \right) \right. \\ &\quad \left. - 2 \left( (31.63536831 \text{ eV}) \sqrt{\frac{2\hbar \sqrt{\frac{3}{4} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2}} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \right\} \quad (13.522) \\ &= -49.66493 \text{ eV} - 2 \left( 0.25493 \text{ eV} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \end{aligned}$$

From Eqs. (13.518-13.522), the total energy of  $^{12}\text{CH}_2$  is

$$\begin{aligned} E_{T+osc}(^{12}\text{CH}_2) &= -49.66493 \text{ eV} + \bar{E}_{osc}(^{12}\text{CH}_2) \\ &= -49.66493 \text{ eV} - 2 \left( 0.25493 \text{ eV} - \frac{1}{2} (0.35532 \text{ eV}) \right) \\ &= -49.81948 \text{ eV} \end{aligned} \quad (13.523)$$

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

$^{12}\text{CH}_2$  has the same electronic configuration as  $^{14}\text{NH}$ . The dissociation of the bond of the dihydrogen carbide radical forms a free hydrogen atom with one unpaired electron and a  $\text{C}2sp^3$  HO with three unpaired electrons as shown in Eq. (13.422) wherein the magnetic moments cannot all cancel. Thus, the bond dissociation of  $^{12}\text{CH}_2$  gives rise to  $^{12}\text{CH}$  with the same electronic configuration as  $N$  as given by Eq. (10.134). The  $N$  configuration is more stable than  $H$  as shown in Eqs. (10.141-10.143). The lowering of the energy of the reactants decreases the bond energy. The total energy of carbon is reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.424):

$$E(\text{magnetic}) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_{2sp^3})^3} = \frac{8\pi\mu_0 \mu_B^2}{(0.91771 a_0)^3} = 0.14803 \text{ eV} \quad (13.524)$$

The  $CH_2$  bond dissociation energy,  $E_D(^{12}CH_2)$ , is given by the sum of the total energies of the  $CH$  radical and the hydrogen atom minus the sum of  $E_{T+osc}(^{12}CH_2)$  and  $E(magnetic)$ :

$$E_D(^{12}CH_2) = E(^{12}CH) + E(H) - E_{T+osc}(^{12}CH_2) - E(magnetic) \quad (13.525)$$

where  $E_T(^{12}CH)$  is given by the sum of the energies of the  $C2sp^3$  HO,  $E(C, 2sp^3)$  given by Eq. (13.428),  $E_D(H)$  given by Eq. (13.154), and the negative of the bond energy of  $^{12}CH$  given by Eq. (13.489):

$$E(^{12}CH) = -13.59844 \text{ eV} - 14.63489 \text{ eV} - 3.47 \text{ eV} = -31.70333 \text{ eV} \quad (13.526)$$

Thus, the  $^{12}CH_2$  bond dissociation energy,  $E_D(^{12}CH_2)$ , given by Eqs. (13.154), and (13.523-13.526) is

$$\begin{aligned} E_D(^{12}CH_2) &= -(31.70333 \text{ eV} + 13.59844 \text{ eV}) - (E_{T+osc}(^{12}CH_2) + E(magnetic)) \\ &= -45.30177 \text{ eV} - (-49.81948 \text{ eV} + 0.14803 \text{ eV}) \\ &= 4.36968 \text{ eV} \end{aligned} \quad (13.527)$$

The experimental  $^{12}CH_2$  bond dissociation energy is [39]

$$E_D(^{12}CH_2) = 4.33064 \text{ eV} \quad (13.528)$$

## 15 BOND ANGLE OF $^{12}CH_2$

The  $CH_2$  MO comprises a linear combination of two  $C-H$ -bond MOs. Each  $C-H$ -bond MO comprises the superposition of a  $H_2$ -type ellipsoidal MO and the  $C2sp^3$  HO with a relative charge density of 0.75 to 1.25; otherwise, the  $C2sp^3$  shell is unchanged. A bond is also possible between the two H atoms of the  $C-H$  bonds. Such  $H-H$  bonding would decrease the  $C-H$  bond strength since electron density would be shifted from the  $C-H$  bonds to the  $H-H$  bond. Thus, the bond angle between the two  $C-H$  bonds is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal H atoms of the  $C-H$  bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the  $H-H$  ellipsoidal MO is

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \quad (13.529)$$

The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \quad (13.530)$$

The length of the semiminor axis of the prolate spheroidal  $H-H$  MO  $b=c$  is given by Eq. (13.62).

The bond angle of  $CH_2$  is derived by using the orbital composition and an energy matching factor as in the case with  $NH_2$  and  $NH_3$ . Since the two  $H_2$ -type ellipsoidal MOs comprise 75% of the  $H$  electron density of  $H_2$  and the energy of each  $H_2$ -type ellipsoidal MO is matched to that of the  $C2sp^3$  HO; the component energies and the total energy  $E_T$  of the  $H-H$  bond are given by Eqs. (13.67-13.73) except that  $V_e$ ,  $T$ , and  $V_m$  are corrected for the hybridization-energy-matching factor of 0.91771 given by Eq. (13.430). Substitution of Eq. (13.529) into Eq. (13.233) with the hybridization factor gives

$$0 = \left[ \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left[ (0.91771)^{-1} \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 a^3} \frac{m_e}{m_e c^2}} \right] \right. \\ \left. + \frac{1}{2} \hbar \sqrt{\frac{0.75e^2}{8\pi\epsilon_0 a^3} - \frac{e^2}{8\pi\epsilon_0 (a+c')^3}} \right] \frac{1}{0.5m_p} \quad (13.531)$$

From the energy relationship given by Eq. (13.531) and the relationship between the axes given by Eqs. (13.529-13.530) and (13.62-13.63), the dimensions of the  $H-H$  MO can be solved.

The most convenient way to solve Eq. (13.531) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 5.1500a_0 = 2.7253 \times 10^{-10} \text{ m} \quad (13.532)$$

Substitution of Eq. (13.532) into Eq. (13.529) gives

$$c' = 1.6047a_0 = 8.4916 \times 10^{-11} \text{ m} \quad (13.533)$$

The internuclear distance given by multiplying Eq. (13.533) by two is

$$2c' = 3.2094a_0 = 1.6983 \times 10^{-10} \text{ m} \quad (13.534)$$

Substitution of Eqs. (13.532-13.533) into Eq. (13.62) gives

$$b = c = 4.8936a_0 = 2.5896 \times 10^{-10} \text{ m} \quad (13.535)$$



Substitution of Eqs. (13.532-13.533) into Eq. (13.63) gives

$$e = 0.3116 \quad (13.536)$$

Using,  $2c'_{H-H}$  (Eq. (13.534)), the distance between the two  $H$  atoms when the total energy of the corresponding MO is zero (Eq. (13.531)), and  $2c'_{C-H}$  (Eq. (13.501)), the internuclear distance of each  $C-H$  bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle  $\theta$  between the  $C-H$  bonds is

$$\theta = \cos^{-1} \left( \frac{2(2.09132)^2 - (3.2094)^2}{2(2.09132)^2} \right) = \cos^{-1}(-0.1775) = 100.22^\circ \quad (13.537)$$

The experimental angle between the  $C-H$  bonds is [38]

$$\theta = 102.4^\circ \quad (13.538)$$

10 The results of the determination of bond parameters of  $CH_2$  are given in Table 13.1.

The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## 15 METHYL RADICAL ( $CH_3$ )

The methyl radical  $CH_3$  is formed by the reaction of a hydrogen atom with a dihydrogen carbide radical:



20  $CH_3$  can be solved using the same principles as those used to solve and  $NH_3$  with the exception that the carbon  $2s$  and  $2p$  shells hybridize to form a single  $2sp^3$  shell as an energy minimum. Three diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with three carbon  $2sp^3$  hybridized orbitals (HOs) to form  
25 the MO of  $CH_3$ . The solution is very similar to that of  $CH_2$  except that there are three  $CH$  bonds in  $CH_3$ .

FORCE BALANCE OF  $CH_3$ 

$CH_3$  comprises three chemical bonds between carbon and hydrogen atoms. Each  $C-H$  bond comprises two spin-paired electrons with one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom. Each  $H$ -atom electron forms a  
 5  $H_2$ -type ellipsoidal MO with an unpaired  $C$ -atom electrons. However, such a bond is not possible with the outer two  $C$  electrons in their ground state since the resulting  $H_2$ -type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon  $2p$  shell which is not energetically stable, and only two electrons are unpaired. Thus, when bonding the carbon  $2s$  and  $2p$  shells hybridize to form a single  $2sp^3$  shell as an energy  
 10 minimum. The electron configuration and the energy,  $E(C, 2sp^3)$ , of the  $C2sp^3$  shell is given by Eqs. (13.422), and (13.428), respectively.

For each  $C-H$  bond, a  $C2sp^3$  electron combines with the  $H1s$  electron to form a molecular orbital. The proton of the  $H$  atom and the nucleus of the  $C$  atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , each of the three  $C-H$ -bond  
 15 MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the  $H$  proton that is continuous with the  $C2sp^3$  shell at the  $C$  atom whose nucleus serves as the other focus. The radius and the energy of the  $C2sp^3$  shell are unchanged with bond  
 20 formation. The central paramagnetic force due to spin of each  $C-H$  bond is provided by the spin-pairing force of the  $CH_3$  MO that has the symmetry of an  $s$  orbital that superimposes with the  $C2sp^3$  orbitals such that the corresponding angular momenta are unchanged.

The energies in the  $CH_3$  MO involve only each  $C2sp^3$  and each  $H1s$  electron with  
 25 the formation of each  $C-H$  bond. The sum of the energies of the  $H_2$ -type ellipsoidal MOs is matched to that of the  $C2sp^3$  shell. As in the cases with of  $OH$ ,  $H_2O$ ,  $NH$ ,  $NH_2$ ,  $NH_3$ ,  $CH$ , and  $CH_2$  the linear combination of each  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  HO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the  $C2sp^3$  HO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $CH_3$  MO must

comprise three  $C-H$  bonds with each comprising 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO:



5

The force balance of the  $CH_3$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.540) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant  $k'$  to determine the ellipsoidal parameter  $c'$  of the each  $H_2$ -type-  
 10 ellipsoidal-MO component of the  $CH_3$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each  $C-H$ -bond MO to each focus  $c'$  is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal  $C-H$ -bond MO  $b = c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for  
 15 the solution of the other axes of each prolate spheroid and eccentricity of each  $C-H$ -bond MO. Since each of the three prolate spheroidal  $C-H$ -bond MOs comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $C2sp^3$  HO, the energy  $E(C, 2sp^3)$  in Eq. (13.428) adds to that of the three corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $CH_3$  MO. From the energy equation and the relationship between the axes, the dimensions  
 20 of the  $CH_3$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ ,  $T$ , and  $V_m$  are three times those of  $CH$  corresponding to the three  $C-H$  bonds. Since the each prolate spheroidal  $H_2$ -type MO transitions to the  $C2sp^3$  HO and the energy of the  $C2sp^3$  shell must remain constant and equal to the  $E(C, 2sp^3)$  given by Eq. (13.428), the total energy  $E_T(CH_3)$  of the  $CH_3$  MO is  
 25 given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C2sp^3$  HO and the three  $H_2$ -type ellipsoidal MOs that forms the  $CH_3$  MO as given by Eq. (13.540). Using Eq. (13.431),  $E_T(CH_3)$  is given by

$$\begin{aligned}
 E_T(CH_3) &= E_T + E(C, 2sp^3) \\
 &= -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV}
 \end{aligned} \tag{13.541}$$

The three hydrogen atoms and the hybridized carbon atom can achieve an energy minimum as a linear combination of three  $H_2$ -type ellipsoidal MOs each having the proton and the carbon nucleus as the foci. Hybridization gives rise to the  $C2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  given by Eq. (13.435). To meet the equipotential condition of the union of the  $H_2$ -type-ellipsoidal-MO and the  $C2sp^3$  HO, the electron energies in Eqs. (13.431), (13.495), and (13.541) were normalized by the ratio of 14.82575 eV, the magnitude of  $E_{Coulomb}(C, 2sp^3)$  given by Eq. (13.425), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). The factor given by Eq. (13.430) normalized the energies to match that of the Coulombic energy alone to meet the energy matching condition of each  $C-H$ -bond MO under the influence of the proton and the  $C$  nucleus. Each  $C-H$ -bond MO comprises the same  $C2sp^3$  shell having its energy normalized to that of the Coulombic energy between the electron and a charge of  $+e$  at the carbon focus of the  $CH_3$  MO. Thus, the energy of the  $CH_3$  MO is also given by the sum of that of the three  $H_2$ -type ellipsoidal MOs given by Eq. (11.212) minus two times the Coulombic energy,  $E_{Coulomb}(H) = -13.605804 \text{ eV}$ , of the two redundant  $+e$ 's of the linear combination:

$$\begin{aligned}
 E_T(3H_2 - 2H) &= -\frac{3e^2}{8\pi\epsilon_0 a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] - 2E_{Coulomb}(H) \\
 &= 3(-31.63536831 \text{ eV}) - 2(-13.605804 \text{ eV}) \\
 &= -67.69450 \text{ eV}
 \end{aligned} \tag{13.542}$$

$E_T(CH_3)$  given by Eq. (13.541) is set equal to three times the energy of the  $H_2$ -type ellipsoidal MO minus two times the Coulombic energy of  $H$  given by Eq. (13.542):

$$E_T(CH_3) = -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} = -67.69450 \text{ eV} \tag{13.543}$$

From the energy relationship given by Eq. (13.543) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH_3$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.543) gives

$$\frac{3e^2}{8\pi\epsilon_0\sqrt{\frac{2aa_0}{3}}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right] = e53.05961 \quad (13.544)$$

5 The most convenient way to solve Eq. (13.544) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.62893a_0 = 8.61990 \times 10^{-11} \text{ m} \quad (13.545)$$

Substitution of Eq. (13.545) into Eq. (13.60) gives

$$c' = 1.04209a_0 = 5.51450 \times 10^{-11} \text{ m} \quad (13.546)$$

10 The internuclear distance given by multiplying Eq. (13.546) by two is

$$2c' = 2.08418a_0 = 1.10290 \times 10^{-10} \text{ m} \quad (13.547)$$

The experimental bond distance is [38]

$$2c' = 1.079 \times 10^{-10} \text{ m} \quad (13.548)$$

Substitution of Eqs. (13.545-13.546) into Eq. (13.62) gives

$$15 \quad b = c = 1.25198a_0 = 6.62518 \times 10^{-11} \text{ m} \quad (13.549)$$

Substitution of Eqs. (13.545-13.546) into Eq. (13.63) gives

$$e = 0.63974 \quad (13.550)$$

The nucleus of the  $H$  atom and the nucleus of the  $C$  atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of each  $H_2$ -type ellipsoidal

20 MO and the  $C2sp^3$  HO are given by Eqs. (13.84-13.95), (13.261-13.270), and (13.434-13.442). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{2sp^3} = 0.91771a_0$  is the radius of the  $C2sp^3$  shell. Substitution of Eqs. (13.545-13.546) into Eq. (13.261) gives

$$\theta' = 85.65^\circ \quad (13.551)$$

25 Then, the angle  $\theta_{C2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C2sp^3HO} = 180^\circ - 85.65^\circ = 94.35^\circ \quad (13.552)$$

as shown in Figure 14. The angle  $\theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  radial vector given by Eqs. (13.442-13.443), (13.549), and (13.552) is

$$\theta_{H_2MO} = 46.96^\circ \quad (13.553)$$

5 Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.445), (13.545), and (13.553) is

$$d_{H_2MO} = 1.11172a_0 = 5.88295 \times 10^{-11} \text{ m} \quad (13.554)$$

The distance  $d_{C2sp^3HO}$  along the internuclear axis from the origin of the  $C$  atom to the point  
10 of intersection of the orbitals given by Eqs. (13.447), (13.546), and (13.554) is

$$d_{C2sp^3HO} = 0.06963a_0 = 3.68457 \times 10^{-12} \text{ m} \quad (13.555)$$

As shown in Eq. (13.540), the uniform charge-density in the  $C2sp^3$  HO is increased by a factor of 0.25 and the  $H$ -atom density is decreased by a factor of 0.25 for by each  $C-H$  bond. Using the orbital composition of  $CH_3$  (Eq. (13.540)), the radii of  
15  $C1s = 0.17113a_0$  (Eq. (10.51)) and  $C2sp^3 = 0.91771a_0$  (Eq. (10.424)) shells, and the parameters of the  $CH_3$  MO given by Eqs. (13.3-13.4), (13.545-13.547), and (13.549-13.555), the charge-density of the  $CH_3$  MO comprising the linear combination of three  $C-H$ -bond MOs is shown in Figure 17. Each  $C-H$ -bond MO comprises a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO having the dimensional diagram shown in Figure 14.

20

### ENERGIES OF $CH_3$

The energies of  $CH_3$  are three times those of  $CH$  and are given by the substitution of the semiprincipal axes (Eqs. (13.545-13.546) and (13.549)) into the energy equations Eq. (13.541) and (Eqs. (13.449-13.452)) that are multiplied by three:

$$25 \quad V_e = 3(0.91771) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -108.94944 \text{ eV} \quad (13.556)$$

$$V_p = \frac{3e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 39.16883 \text{ eV} \quad (13.557)$$

$$T = 3(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 33.44213 \text{ eV} \quad (13.558)$$

$$V_m = 3(0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -16.72107 \text{ eV} \quad (13.559)$$

$$E_T(CH_3) = -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.63489 \text{ eV} = -67.69444 \text{ eV} \quad (13.560)$$

5 where  $E_T(CH_3)$  is given by Eq. (13.541) which is reiteratively matched to Eq. (13.542) within five-significant-figure-round-off-error.

### VIBRATION OF $CH_3$

The vibrational energy levels of  $CH_3$  may be solved as three equivalent coupled harmonic  
 10 oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

### 15 THE DOPPLER ENERGY TERMS OF $^{12}CH_3$

The reentrant oscillation of hybridized orbitals in the transition state is not coupled. Therefore, the equations of the radiation reaction force of methyl radical are the same as those of the corresponding hydrogen carbide radicals with the substitution of the methyl radical parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the  
 20 reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 2.55577 \times 10^{16} \text{ rad/s} \quad (13.561)$$

where  $b$  is given by Eq. (13.549). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.55577 \times 10^{16} \text{ rad/s} = 16.82249 \text{ eV} \quad (13.562)$$

25 In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic

energy given by Eq. (13.562) for  $\bar{E}_K$  gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(16.82249 \text{ eV})}{m_e c^2}} = -0.25670 \text{ eV} \quad (13.563)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $CH_3$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (13.563) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of each  $C-H$  bond. Using  $\omega_e$  given by Eq. (13.458) for  $\bar{E}_{Kvib}$  of the transition state having three independent bonds,  $\bar{E}'_{osc} (^{12}CH_3)$  per bond is

$$\bar{E}'_{osc} (^{12}CH_3) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.564)$$

$$\bar{E}'_{osc} (^{12}CH_3) = -0.25670 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) = -0.07904 \text{ eV} \quad (13.565)$$

Given that the vibration and reentrant oscillation is for three  $C-H$  bonds,  $\bar{E}_{osc} (^{12}CH_3)$ , is:

$$\begin{aligned} \bar{E}_{osc} (^{12}CH_3) &= 3 \left( \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \\ &= 3 \left( -0.25670 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) \right) \\ &= -0.23711 \text{ eV} \end{aligned} \quad (13.566)$$

15

#### TOTAL AND BOND ENERGIES OF $^{12}CH_3$

$E_{T+osc} (^{12}CH_3)$ , the total energy of the  $^{12}CH_3$  radical including the Doppler term, is given by the sum of  $E_T (CH_3)$  (Eq. (13.543)) and  $\bar{E}_{osc} (^{12}CH_3)$  given by Eq. (13.566):

$$\begin{aligned} E_{T+osc} (CH_3) &= V_e + T + V_m + V_p + E(C, 2sp^3) + \bar{E}_{osc} (^{12}CH_3) \\ &= E_T (CH_3) + \bar{E}_{osc} (^{12}CH_3) \end{aligned} \quad (13.567)$$



$$E_{T+osc}({}^{12}\text{CH}_3) = \left\{ \left( \frac{-3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} \right) \right. \\ \left. - 3 \left( (31.63536831 \text{ eV}) \sqrt{\frac{2\hbar \sqrt{\frac{3}{4} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2}} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \right\} \quad (13.568)$$

$$= -67.69450 \text{ eV} - 3 \left( 0.25670 \text{ eV} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$

From Eqs. (13.564-13.568), the total energy of  ${}^{12}\text{CH}_3$  is

$$E_{T+osc}({}^{12}\text{CH}_3) = -67.69450 \text{ eV} + \bar{E}_{osc}({}^{12}\text{CH}_3) \\ = -67.69450 \text{ eV} - 3 \left( 0.25670 \text{ eV} - \frac{1}{2} (0.35532 \text{ eV}) \right) \quad (13.569) \\ = -67.93160 \text{ eV}$$

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

5 The  $\text{CH}_3$  bond dissociation energy,  $E_D({}^{12}\text{CH}_3)$ , is given by the sum of the total energies of the  $\text{CH}_2$  radical and the hydrogen atom minus  $E_{T+osc}({}^{12}\text{CH}_3)$ :

$$E_D({}^{12}\text{CH}_3) = E({}^{12}\text{CH}_2) + E(\text{H}) - E_{T+osc}({}^{12}\text{CH}_3) \quad (13.570)$$

where  $E_T({}^{12}\text{CH}_2)$  is given by the sum of the energies of the  $\text{C}2sp^3$  HO,  $E(\text{C}, 2sp^3)$  given by Eq. (13.428),  $2E_D(\text{H})$  given by Eq. (13.154), and the negative of the bond energies of  ${}^{12}\text{CH}$  given by Eq. (13.489) and  ${}^{12}\text{CH}_2$  given by Eq. (13.528):

$$E({}^{12}\text{CH}_2) = 2(-13.59844 \text{ eV}) - 14.63489 \text{ eV} - 3.47 \text{ eV} - 4.33064 \text{ eV} = -49.63241 \text{ eV} \quad (13.571)$$

Thus, the  ${}^{12}\text{CH}_3$  bond dissociation energy,  $E_D({}^{12}\text{CH}_3)$ , given by Eqs. (13.154), and (13.569-13.571) is

$$E_D({}^{12}\text{CH}_3) = -(-49.63241 \text{ eV} - 13.59844 \text{ eV}) - E_{T+osc}({}^{12}\text{CH}_3) \\ = -63.23085 \text{ eV} - (-67.93160 \text{ eV}) \quad (13.572) \\ = 4.70075 \text{ eV}$$

The experimental  ${}^{12}\text{CH}_3$  bond dissociation energy is [40]

$$E_D({}^{12}\text{CH}_3) = 4.72444 \text{ eV} \quad (13.573)$$

BOND ANGLE OF  $^{12}\text{CH}_3$ 

Using,  $2c'_{H-H}$  (Eq. (13.534)), the distance between the two  $H$  atoms when the total energy of the corresponding MO is zero (Eq. (13.531)), and  $2c'_{C-H}$ , the internuclear distance of each  $C-H$  bond (Eq. (13.547)), the corresponding bond angle can be determined from the law of cosines. Using Eq. (13.537), the bond angle  $\theta$  between the  $C-H$  bonds is

$$\begin{aligned}\theta &= \cos^{-1} \left( \frac{2(2.08418)^2 - (3.2094)^2}{2(2.08418)^2} \right) \\ &= \cos^{-1}(-0.18560) \\ &= 100.70^\circ\end{aligned}\tag{13.574}$$

The  $\text{CH}_3$  radical has a pyramidal structure with the carbon atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. The distance  $d_{\text{origin}-H}$  from the origin to the nucleus of a hydrogen atom given by Eqs. (13.534) and (13.412) is

$$d_{\text{origin}-H} = 1.85293a_0\tag{13.575}$$

The height along the z-axis of the pyramid from the origin to  $C$  nucleus  $d_{\text{height}}$  given by Eqs. (13.414), (13.547), and (13.575) is

$$d_{\text{height}} = 0.95418a_0\tag{13.576}$$

The angle  $\theta_v$  of each  $C-H$  bond from the z-axis given by Eqs. (13.416), (13.575), and (13.576) is

$$\theta_v = 62.75^\circ\tag{13.577}$$

The  $\text{CH}_3$  MO shown in Figure 17 was rendered using these parameters.

The results of the determination of bond parameters of  $\text{CH}_3$  are given in Table 13.1.

The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

METHANE MOLECULE ( $\text{CH}_4$ )

The methane molecule  $\text{CH}_4$  is formed by the reaction of a hydrogen atom with a methyl radical:



$CH_4$  can be solved using the same principles as those used to solve and  $CH_3$  wherein the carbon  $2s$  and  $2p$  shells hybridize to form a single  $2sp^3$  shell as an energy minimum. Four diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with four carbon  $2sp^3$  hybridized orbitals (HOs) to form the MO of  $CH_4$ . The solution is very similar to that of  $CH_3$  except that there are four  $CH$  bonds in  $CH_4$ . Methane is the simplest hydrocarbon that can be solved using the results for  $CH_3$ . From the solution of  $CH_2$  as well as  $CH_3$ , more complex hydrocarbons can be solved using these radical as basis elements with bonding between the  $C2sp^3$  hybridized carbons.

10

#### FORCE BALANCE OF $CH_4$

$CH_4$  comprises four chemical bonds between carbon and hydrogen atoms. Each  $C-H$  bond comprises two spin-paired electrons with one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom. Each  $H$ -atom electron forms a  $H_2$ -type ellipsoidal MO with an unpaired  $C$ -atom electrons. However, such a bond is not possible with the outer two  $C$  electrons in their ground state since the resulting  $H_2$ -type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon  $2p$  shell which is not energetically stable, and only two electrons are unpaired. Thus, when bonding the carbon  $2s$  and  $2p$  shells hybridize to form a single  $2sp^3$  shell as an energy minimum. The electron configuration and the energy,  $E(C, 2sp^3)$ , of the  $C2sp^3$  shell is given by Eqs. (13.422), and (13.428), respectively.

For each  $C-H$  bond, a  $C2sp^3$  electron combines with the  $H1s$  electron to form a molecular orbital. The proton of the  $H$  atom and the nucleus of the  $C$  atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , each of the four  $C-H$ -bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the  $H$  proton that can be solve as being continuous with the  $C2sp^3$  shell at the  $C$  atom whose nucleus serves as the other focus. The radius and the energy of the  $C2sp^3$  shell are

unchanged with bond formation. The central paramagnetic force due to spin of each  $C-H$  bond is provided by the spin-pairing force of the  $CH_4$  MO that has the symmetry of an  $s$  orbital that superimposes with the  $C2sp^3$  orbitals such that the corresponding angular momenta are unchanged.

5 The energies in the  $CH_4$  MO involve only each  $C2sp^3$  and each  $H1s$  electron with the formation of each  $C-H$  bond. The sum of the energies of the  $H_2$ -type ellipsoidal MOs is matched to that of the  $C2sp^3$  shell. As in the cases with of  $OH$ ,  $H_2O$ ,  $NH$ ,  $NH_2$ ,  $NH_3$ ,  $CH$ ,  $CH_2$ , and  $CH_3$  the  $CH_4$ , the  $CH_4$  MO must comprise four  $C-H$  bonds with each having 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO in a linear combination in order to  
10 match potential, kinetic, and orbital energy relationships:

$$4[1 C2sp^3 + 0.75 H_2 MO] \rightarrow CH_4 MO \quad (13.579)$$

The force balance of the  $CH_4$  MO is determined by the boundary conditions that arise from  
15 the linear combination of orbitals according to Eq. (13.579) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant  $k'$  to determine the ellipsoidal parameter  $c'$  of the each  $H_2$ -type-ellipsoidal-MO component of the  $CH_4$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each  $C-H$ -bond MO to each focus  $c'$  is  
20 given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal  $C-H$ -bond MO  $b = c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of each  $C-H$ -bond MO. Since each of the four prolate spheroidal  $C-H$ -bond MOs comprises a  $H_2$ -type-  
25 ellipsoidal MO that transitions to the  $C2sp^3$  HO, the energy  $E(C, 2sp^3)$  in Eq. (13.428) adds to that of the four corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $CH_4$  MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH_4$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ ,  $T$ , and  $V_m$  are four times those of  $CH$  corresponding to the four  $C-H$  bonds. Since the each prolate spheroidal  $H_2$ -type MO transitions to the  $C2sp^3$  HO and the energy of the  $C2sp^3$  shell must remain constant and equal to the  $E(C, 2sp^3)$  given by Eq. (13.428), the total energy  $E_T(CH_4)$  of the  $CH_4$  MO is  
 5 given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C2sp^3$  HO and the four  $H_2$ -type ellipsoidal MOs that forms the  $CH_4$  MO as given by Eq. (13.579). Using Eq. (13.431),  $E_T(CH_4)$  is given by

$$\begin{aligned} E_T(CH_4) &= E_T + E(C, 2sp^3) \\ &= -\frac{4e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} \end{aligned} \quad (13.580)$$

The four hydrogen atoms and the hybridized carbon atom can achieve an energy minimum as  
 10 a linear combination of four  $H_2$ -type ellipsoidal MOs each having the proton and the carbon nucleus as the foci. Hybridization gives rise to the  $C2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  given by Eq. (13.435). To meet the equipotential condition of the union of the  $H_2$ -type-ellipsoidal-MO and the  $C2sp^3$  HO, the electron energies in Eqs. (13.431), (13.495), (13.541), and (13.580) were normalized by the ratio of 14.82575 eV, the  
 15 magnitude of  $E_{Coulomb}(C, 2sp^3)$  given by Eq. (13.425), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). The factor given by Eq. (13.430) normalized the energies to match that of the Coulombic energy alone to meet the energy matching condition of each  $C-H$ -bond MO under the influence of the proton and the  $C$  nucleus. Each  $C-H$ -bond MO comprises the same  $C2sp^3$  shell  
 20 having its energy normalized to that of the Coulombic energy between the electron and a charge of  $+e$  at the carbon focus of the  $CH_4$  MO. Thus, the energy of the  $CH_4$  MO is also given by the sum of that of the four  $H_2$ -type ellipsoidal MOs given by Eq. (11.212) minus three times the Coulombic energy,  $E_{Coulomb}(H) = -13.605804 \text{ eV}$ , of the three redundant  $+e$ 's of the linear combination:

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$$\begin{aligned}
 E_T(4H_2 - 3H) &= -\frac{4e^2}{8\pi\epsilon_0 a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] - 3E_{Coulomb}(H) \\
 &= 4(-31.63536831 \text{ eV}) - 3(-13.605804 \text{ eV}) \\
 &= -85.72406 \text{ eV}
 \end{aligned} \tag{13.581}$$

$E_T(CH_4)$  given by Eq. (13.580) is set equal to four times the energy of the  $H_2$ -type ellipsoidal MO minus three times the Coulombic energy of  $H$  given by Eq. (13.581):

$$E_T(CH_4) = -\frac{4e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} = -85.72406 \text{ eV} \tag{13.582}$$

5

From the energy relationship given by Eq. (13.582) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH_4$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.543) gives

$$\frac{4e^2}{8\pi\epsilon_0 \sqrt{\frac{2aa_0}{3}}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right] = e71.08917 \tag{13.583}$$

10 The most convenient way to solve Eq. (13.583) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.62340a_0 = 8.59066 \times 10^{-11} \text{ m} \tag{13.584}$$

Substitution of Eq. (13.584) into Eq. (13.60) gives

$$c' = 1.04032a_0 = 5.50514 \times 10^{-11} \text{ m} \tag{13.585}$$

15 The internuclear distance given by multiplying Eq. (13.585) by two is

$$2c' = 2.08064a_0 = 1.10103 \times 10^{-10} \text{ m} \tag{13.586}$$

The experimental bond distance is [41]

$$2c' = 1.087 \times 10^{-10} \text{ m} \tag{13.587}$$

Substitution of Eqs. (13.584-13.585) into Eq. (13.62) gives

$$20 \quad b = c = 1.24626a_0 = 6.59492 \times 10^{-11} \text{ m} \tag{13.588}$$

Substitution of Eqs. (13.584-13.585) into Eq. (13.63) gives

$$e = 0.64083 \tag{13.589}$$

The nucleus of the  $H$  atom and the nucleus of the  $C$  atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of each  $H_2$ -type ellipsoidal

MO and the  $C2sp^3$  HO in the absence of the other three are given by Eqs. (13.84-13.95), (13.261-13.270), (13.434-13.442), and (13.551-13.555). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{2sp^3} = 0.91771a_0$  is the radius of the  $C2sp^3$  shell. Substitution of Eqs. (13.584-13.585) into Eq. (13.261) gives

$$5 \quad \theta' = 86.20^\circ \quad (13.590)$$

Then, the angle  $\theta_{C2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C2sp^3HO} = 180^\circ - 86.20^\circ = 93.80^\circ \quad (13.591)$$

as shown in Figure 14. The angle  $\theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  radial vector given by Eqs. (13.442-13.443), (13.588), and (13.591) is

$$10 \quad \theta_{H_2MO} = 47.29^\circ \quad (13.592)$$

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.445), (13.584), and (13.592) is

$$15 \quad d_{H_2MO} = 1.10121a_0 = 5.82734 \times 10^{-11} \text{ m} \quad (13.593)$$

The distance  $d_{C2sp^3HO}$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals given by Eqs. (13.447), (13.585), and (13.593) is

$$d_{C2sp^3HO} = 0.06089a_0 = 3.22208 \times 10^{-12} \text{ m} \quad (13.594)$$

20 The  $H_2$ -type ellipsoidal MOs do not actually directly contact the  $C2sp^3$  HO. As discussed in the Force Balance of  $H_2O$  section, with the addition of the fourth C-H bond, the  $H_2$ -type ellipsoidal MOs may linearly combine to form a continuous two-dimensional surface of equipotential equivalent to that of the MOs if they did contact the  $C2sp^3$  HO. However, Eqs. (13.579-13.580) must hold based on conservation of momentum and the  
25 potential, kinetic, and total energy relationships. In order that there is current continuity given the constraints of Eqs. (13.579-13.580), the existence of a self-contained, continuous-current, linear-combination of the  $H_2$ -type ellipsoidal MOs requires that electrons are divisible between the combination  $H_2$ -type MO and the  $C2sp^3$  HO. This is not possible. Thus, at the points of intersection of the  $H_2$ -type MOs of methane, symmetry, electron

indivisibility, current continuity, and conservation of energy and angular momentum require that the current between the  $C2sp^3$  shell and points of mutual contact is projected onto and flows along the radial vector to the surface of  $C2sp^3$  shell. This current designated the bisector current (BC) meets the  $C2sp^3$  surface and does not travel to distances shorter than its radius. Moreover, an energy minimum is obtained when the  $H$ -atom charge-density of each  $C-H$ -bond MO is decreased by a factor of 0.25 with a corresponding 0.25 increase in that of the three other  $C-H$ -bond MOs. In this case, the angular momentum components of the transferred current mutually cancel. The geometry of the equivalent bonds is tetrahedral. The symmetry point group is  $T_d$ . This geometry is equivalent to the indistinguishable bonds positioned uniformly on a spherical surface or also at the apexes of a cube. The predicted angle  $\theta$  between the  $C-H$  bonds is

$$\theta = 109.5^\circ \quad (13.595)$$

The experimental bond angle is [41]

$$\theta = 109.5^\circ \quad (13.596)$$

The polar angle  $\phi$  at which the  $H_2$ -type ellipsoidal MOs intersect is given by the bisector of the angle  $\theta$  between the  $C-H$  bonds:

$$\phi = \frac{109.5}{2} = 54.75^\circ \quad (13.597)$$

With the carbon nucleus defined as the origin and one of the  $C-H$  bonds defined as the positive x-axis, the polar-coordinate angle of the intersection occurs at

$$\phi' = 54.75^\circ + 180^\circ = 234.57^\circ \quad (13.598)$$

The polar radius  $r_i$  at this angle is given by Eqs. (13.84-13.85):

$$r_i = (a - c') \frac{1 + \frac{c'}{a}}{1 + \frac{c'}{a} \cos \phi'} \quad (13.599)$$

Substitution of Eqs. (13.584-13.585) and (13.589) into Eq. (13.599) gives

$$r_i = 1.52223a_0 = 8.05530 \times 10^{-11} \text{ m} \quad (13.600)$$

Using the orbital composition of  $CH_4$  (Eq. (13.579)), the radii of  $C1s = 0.17113a_0$  (Eq. (10.51)) and  $C2sp^3 = 0.91771a_0$  (Eq. (10.424)) shells, and the parameters of the  $CH_4$  MO given by Eqs. (13.3-13.4), (13.584-13.586), and (13.588-13.600), the charge-density of the  $CH_4$  MO comprising the linear combination of four  $C-H$ -bond MOs is shown in



Figure 18. Each  $C-H$ -bond MO having the dimensional diagram shown in Figure 14 comprises a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO according to Eq. (13.579). But, based on the  $T_d$  symmetry of the  $H_2$ -type MOs, the charge is distributed 1:1 between the  $H_2$ -type MOs and the  $C2sp^3$  shell.

5

### ENERGIES OF $CH_4$

The energies of  $CH_4$  are four times those of  $CH$  and are given by the substitution of the semiprincipal axes (Eqs. (13.584-13.585) and (13.588)) into the energy equations Eq. (13.580) and (Eqs. (13.449-13.452)) that are multiplied by four:

$$10 \quad V_e = 4(0.91771) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -145.86691 \text{ eV} \quad (13.601)$$

$$V_p = \frac{4e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 52.31390 \text{ eV} \quad (13.602)$$

$$T = 4(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 44.92637 \text{ eV} \quad (13.603)$$

$$V_m = 4(0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -22.46318 \text{ eV} \quad (13.604)$$

$$E_T(CH_4) = -\frac{4e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} = -85.72472 \text{ eV} \quad (13.605)$$

15

where  $E_T(CH_4)$  is given by Eq. (13.580) which is reiteratively matched to Eq. (13.581) within five-significant-figure round-off error.

### VIBRATION OF $CH_4$

20 The vibrational energy levels of  $CH_4$  may be solved as four equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

25

THE DOPPLER ENERGY TERMS OF  $^{12}\text{CH}_4$ 

The reentrant oscillation of hybridized orbitals in the transition state is not coupled. Therefore, the equations of the radiation reaction force of methane are the same as those of  $\text{OH}$ ,  $\text{CH}$ ,  $\text{CH}_2$ , and  $\text{CH}_3$  with the substitution of the methane parameters. Using Eqs. 5 (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 2.57338 \times 10^{16} \text{ rad/s} \quad (13.606)$$

where  $b$  is given by Eq. (13.588). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$10 \quad \bar{E}_K = \hbar\omega = \hbar 2.57338 \times 10^{16} \text{ rad/s} = 16.93841 \text{ eV} \quad (13.607)$$

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.607) for  $\bar{E}_K$  gives the Doppler energy of the electrons of each of the four bonds for the reentrant orbit:

$$15 \quad \bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(16.93841 \text{ eV})}{m_e c^2}} = -0.25758 \text{ eV} \quad (13.608)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $\text{CH}_4$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding 20 energies,  $\bar{E}_D$  given by Eq. (13.608) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of each  $\text{C}-\text{H}$  bond. Using  $\omega_e$  given by Eq. (13.458) for  $\bar{E}_{Kvib}$  of the transition state having four independent bonds,  $\bar{E}'_{osc} (^{12}\text{CH}_4)$  per bond is

$$\bar{E}'_{osc} (^{12}\text{CH}_4) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.609)$$

$$\bar{E}'_{osc} (^{12}\text{CH}_4) = -0.25758 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) = -0.07992 \text{ eV} \quad (13.610)$$

The reentrant orbit for the binding of a hydrogen atom to a  $CH_3$  radical involves four  $C-H$  bonds. Since the vibration and reentrant oscillation is along four bonds,  $\bar{E}_{osc}$  for  $^{12}CH_4$ ,  $\bar{E}_{osc}(^{12}CH_4)$ , is:

$$\begin{aligned}\bar{E}_{osc}(^{12}CH_4) &= 4 \left( \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \\ &= 4 \left( -0.25758 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) \right) \\ &= -0.31967 \text{ eV}\end{aligned}\quad (13.611)$$

5

### TOTAL AND BOND ENERGIES OF $^{12}CH_4$

$E_{T+osc}(^{12}CH_4)$ , the total energy of the  $^{12}CH_4$  radical including the Doppler term, is given by the sum of  $E_T(CH_4)$  (Eq. (13.582)) and  $\bar{E}_{osc}(^{12}CH_4)$  given by Eq. (13.611):

$$\begin{aligned}E_{T+osc}(CH_4) &= V_e + T + V_m + V_p + E(C, 2sp^3) + \bar{E}_{osc}(^{12}CH_4) \\ &= E_T(CH_4) + \bar{E}_{osc}(^{12}CH_4)\end{aligned}\quad (13.612)$$

10

$$\begin{aligned}E_{T+osc}(^{12}CH_4) &= \left\{ \left( \frac{-4e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.63489 \text{ eV} \right) \right. \\ &\quad \left. - 4 \left( (31.63536831 \text{ eV}) \sqrt{\frac{2\hbar \sqrt{\frac{3}{4} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}} \right) \right\} \\ &= -85.72406 \text{ eV} - 4 \left( 0.25758 \text{ eV} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)\end{aligned}\quad (13.613)$$

From Eqs. (13.609-13.613), the total energy of  $^{12}CH_4$  is

$$\begin{aligned}E_{T+osc}(^{12}CH_4) &= -85.72406 \text{ eV} + \bar{E}_{osc}(^{12}CH_4) \\ &= -85.72406 \text{ eV} - 4 \left( 0.25758 \text{ eV} - \frac{1}{2} (0.35532 \text{ eV}) \right) \\ &= -86.04373 \text{ eV}\end{aligned}\quad (13.614)$$

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

The  $CH_4$  bond dissociation energy,  $E_D(^{12}CH_4)$ , is given by the sum of the total energies of the  $CH_3$  radical and the hydrogen atom minus  $E_{T+osc}(^{12}CH_4)$ :

$$E_D(^{12}CH_4) = E(^{12}CH_3) + E(H) - E_{T+osc}(^{12}CH_4) \quad (13.615)$$

where  $E_T(^{12}CH_3)$  is given by the sum of the energies of the  $C2sp^3$  HO,  $E(C, 2sp^3)$  given by Eq. (13.428),  $3E_D(H)$  given by Eq. (13.154), and the negative of the bond energies of  $^{12}CH$  given by Eq. (13.489),  $^{12}CH_2$  given by Eq. (13.528), and  $^{12}CH_3$  given by Eq. (13.573):

$$E(^{12}CH_3) = \begin{pmatrix} 3(-13.59844 \text{ eV}) - 14.63489 \text{ eV} \\ -3.47 \text{ eV} - 4.33064 \text{ eV} - 4.72444 \text{ eV} \end{pmatrix} = -67.95529 \text{ eV} \quad (13.616)$$

Thus, the  $^{12}CH_4$  bond dissociation energy,  $E_D(^{12}CH_4)$ , given by Eqs. (13.154), and (13.614-13.616) is

$$\begin{aligned} E_D(^{12}CH_4) &= -(67.95529 \text{ eV} + 13.59844 \text{ eV}) - E_{T+osc}(^{12}CH_4) \\ &= -81.55373 \text{ eV} - (-86.04373 \text{ eV}) \\ &= 4.4900 \text{ eV} \end{aligned} \quad (13.617)$$

The experimental  $^{12}CH_4$  bond dissociation energy is [40]

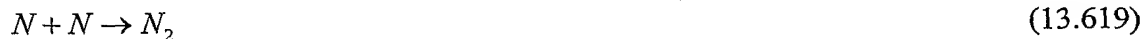
$$E_D(^{12}CH_4) = 4.48464 \text{ eV} \quad (13.618)$$

The results of the determination of bond parameters of  $CH_4$  are given in Table 13.1.

15 The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

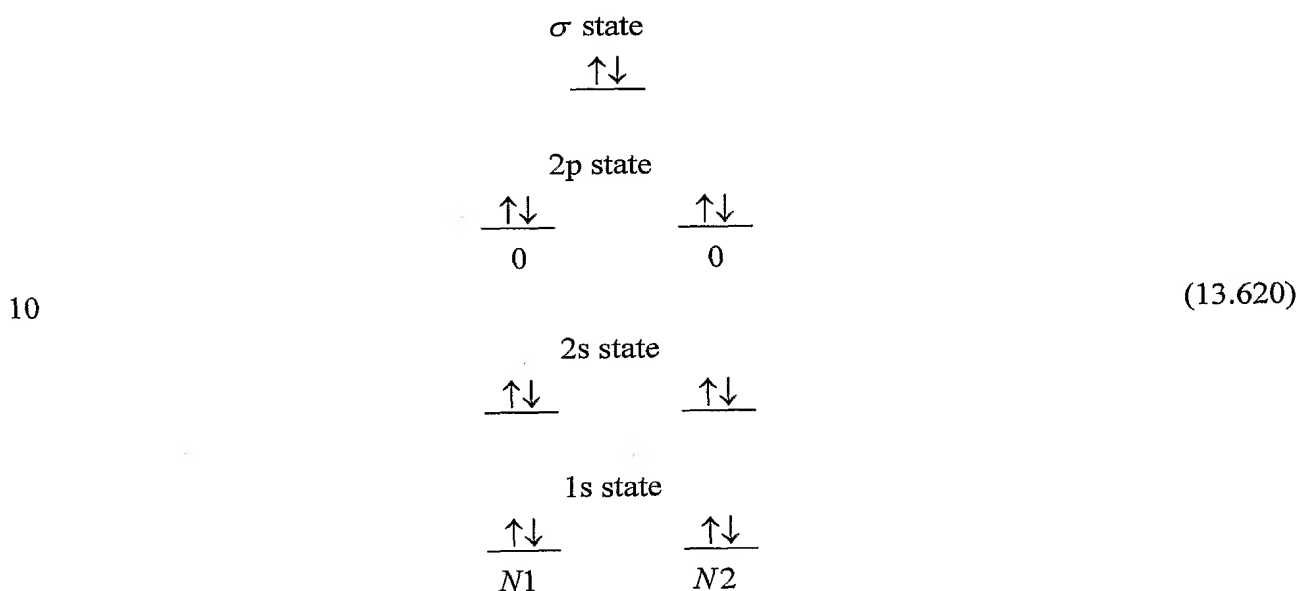
## NITROGEN MOLECULE

20 The nitrogen molecule can be formed by the reaction of two nitrogen atoms:



The bond in the nitrogen molecule comprises a  $H_2$ -type molecular orbital (MO) with two paired electrons. The force balance equation and radius  $r_7$  of the  $2p$  shell of  $N$  is derived in the Seven-Electron Atoms section. With the formation of the  $H_2$ -type MO by the  
25 contribution of a  $2p$  electron from each  $N$  atom, a diamagnetic force arises between the

remaining  $2p$  electrons and the  $H_2$ -type MO. This force from each  $N$  causes the  $H_2$ -type MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining  $2p$  electrons of each  $N$  decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of  $N_2$  is  $1s_1^2 1s_2^2 2s_1^2 2s_2^2 2p_1^2 2p_2^2 \sigma_{1,2}^2$  where the subscript designates the  $N$  atom, 1 or 2,  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is



Nitrogen is predicted to be diamagnetic in agreement with observations [42].

## FORCE BALANCE OF THE $2p$ SHELL OF THE NITROGEN ATOMS OF THE NITROGEN MOLECULE

For each  $N$  atom, force balance for the outermost  $2p$  electron of  $N_2$  (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other  $2p$ -shell as well as the  $2s$ -shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central Coulomb force on the outer-most  $2p$  shell electron of  $N_2$  (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with

the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} \mathbf{i}_r \quad (13.621)$$

for  $r > r_5$ . The  $2p$  shell possess an external electric field given by Eq. (10.92) for  $r > r_6$ . The energy is minimized with conservation of angular momentum. This condition is met  
5 when the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the  $p$ -orbital contribution is the same as that of the reactant nitrogen atoms given by Eq. (10.136) with  $r_6$  replacing  $r_7$ :

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right) \frac{\hbar^2}{4m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r \quad (13.622)$$

And,  $\mathbf{F}_{mag\ 2}$  corresponding to the conserved orbital angular momentum of the three orbitals is given by Eq. (10.89):

$$10 \quad \mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{3\hbar^2}{m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (13.623)$$

The electric field external to the  $2p$  shell given by Eq. (10.92) for  $r > r_6$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the  $p$ -orbital electron having an electric field of +1 outside of its radius is:

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (13.624)$$

15 In addition, the contribution of a  $2p$  electron from each  $N$  atom in the formation of the  $\sigma$  MO gives rise to a paramagnetic force on the remaining two  $2p$  electrons that pair. The force,  $\mathbf{F}_{mag\ 3}$ , follows from Eq. (10.11) wherein the two radii are equal to  $r_6$  and the direction is positive, central:

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \mathbf{i}_r \quad (13.625)$$

20  $\mathbf{F}_{mag\ 3}$  is present in additional diatomic molecules where its contribution minimizes the energy. This AO spin-pairing force reduces the radius directly to reduce the energy, and it can also cancel the contribution of the corresponding electron to  $\mathbf{F}_{diamagnetic}$  to further reduce the energy.

The radius of the  $2p$  shell is calculated by equating the outward centrifugal force to  
25 the sum of the electric (Eq. (13.621)) and diamagnetic (Eqs. (13.622) and (13.624)), and paramagnetic (Eqs. (13.623) and (13.625)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \left( \begin{aligned} & \left( \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{\hbar^2}{12m_e r_6^2 r_3} \sqrt{s(s+1)} + \frac{3\hbar^2}{Zm_e r_6^2 r_3} \sqrt{s(s+1)} \right) \\ & - \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \end{aligned} \right) \quad (13.626)$$

Substitution of  $v_6 = \frac{\hbar}{m_e r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.626) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3} \sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Zm_e r_6^2 r_3} \sqrt{\frac{3}{4}} - \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{\frac{3}{4}} \quad (13.627)$$

5 The quadratic equation corresponding to Eq. (13.627) is

$$r_6^2 - \frac{\frac{\hbar^2}{m_e} \left( 1 - \frac{\sqrt{3}}{8} \right)}{\left( \frac{(Z-5)e^2}{4\pi\epsilon_0} - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} r_6 - \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-5)e^2}{4\pi\epsilon_0} - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} = 0 \quad (13.628)$$

The solution of Eq. (13.628) using the quadratic formula is:

$$r_6 = \frac{a_0 \left( 1 - \frac{\sqrt{3}}{8} \right)}{\left( (Z-5) - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)} \pm a_0 \frac{\sqrt{\left( \frac{1 - \frac{\sqrt{3}}{8}}{\left( (Z-5) - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)} \right)^2 + \frac{20\sqrt{3} \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3}{\left( (Z-5) - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)}}}{2} \quad (13.629)$$

$r_3$  in units of  $a_0$

10 The positive root of Eq. (13.629) must be taken in order that  $r_6 > 0$ . Substitution of

$\frac{r_3}{a_0} = 0.69385$  (Eq. (10.62) with  $Z = 7$ ) into Eq. (13.629) gives

$$r_6 = 0.78402a_0 \quad (13.630)$$

## ENERGIES OF THE $2p$ SHELL OF THE NITROGEN ATOMS OF THE NITROGEN MOLECULE

The central forces on the  $2p$  shell of each  $N$  are increased with the formation of the  $\sigma$  MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms  
5 of the total energy of the two  $N$  atoms at the new radius are calculated and added to the energy of the  $\sigma$  MO to give the total energy of  $N_2$ . Then, the bond energy is determined from the total  $N_2$  energy.

The radius  $r_7$  of each nitrogen atom before bonding is given by Eq. (10.142):

$$r_7 = 0.93084a_0 \quad (13.631)$$

10 Using the initial radius  $r_7$  of each  $N$  atom and the final radius  $r_6$  of the  $N2p$  shell of  $N_2$  (Eq. (13.630)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(N_2, 2p)$  of the Coulombic energy change of the  $N2p$  electrons of both atoms is determined using Eq. (10.102):

$$\begin{aligned} E_T(N_2, 2p) &= -2 \sum_{n=4}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_7} \right) \\ &= -2(13.60580 \text{ eV})(0.20118)(2+3) \\ &= -27.37174 \text{ eV} \end{aligned} \quad (13.632)$$

15

## FORCE BALANCE OF THE $\sigma$ MO OF THE NITROGEN MOLECULE

The  $2p$  shell gives rise to two diamagnetic forces on the  $\sigma$  MO. As given for the hydrogen molecule in the Hydrogen-Type Molecules section, the  $\sigma$  MO comprises two electrons,  $\sigma$  electron 1 and  $\sigma$  electron 2, that are bound at  $\xi = 0$  as a equipotential prolate spheroidal MO  
20 by the central Coulombic field due to the nitrogen atoms at the foci and the spin pairing force on  $\sigma$  electron 2 due to  $\sigma$  electron 1 that initially has smaller semiprincipal axes. The spin-pairing force given in Eq. (11.200) is equal to one half the centrifugal force of the two electrons. The spin-pairing electron of the  $\sigma$  MO is also repelled by the remaining  $2p$  electrons of each  $N$  according to Lenz law, and the force is based on the total number of  
25 these electrons  $n_e$  that interact with the binding  $\sigma$ -MO electron. This diamagnetic force  $F_{\text{diamagneticMO1}}$  is of the same form as the molecular spin-pairing force but in the opposite direction. The force follows from the derivations of Eqs. (10.219) and (11.200) which gives:



$$\mathbf{F}_{\text{diamagneticMO1}} = \frac{n_e \hbar^2}{4m_e a^2 b^2} D \mathbf{i}_\xi \quad (13.633)$$

In addition, there is a relativistically corrected Lorentzian force  $\mathbf{F}_{\text{diamagneticMO2}}$  on the pairing electron of the  $\sigma$  MO that follows from Eqs. (7.15) and (11.200):

$$\mathbf{F}_{\text{diamagneticMO2}} = \frac{1}{Z} \frac{|L| \hbar}{2m_e a^2 b^2} D \mathbf{i}_\xi \quad (13.634)$$

5 where  $|L|$  is the magnitude of the angular momentum of each  $N$  atom at a focus that is the source of the diamagnetism at the  $\sigma$ -MO.

The force balance equation for the  $\sigma$ -MO of the nitrogen molecule given by Eq. (11.200) and Eqs. (13.633-13.634) with  $n_e = 2$  and  $|L| = \hbar$  is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.635)$$

$$10 \quad \frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D - \frac{1}{Z} \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.636)$$

$$\left(2 + \frac{1}{Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D \quad (13.637)$$

$$a = \left(2 + \frac{1}{Z}\right) a_0 \quad (13.638)$$

Substitution of  $Z = 7$  into Eq. (13.638) gives

$$a = 2.14286 a_0 = 1.13395 \times 10^{-10} \text{ m} \quad (13.639)$$

15 Substitution of Eq. (13.639) into Eq. (11.79) is

$$c' = 1.03510 a_0 = 5.47750 \times 10^{-11} \text{ m} \quad (13.640)$$

The internuclear distance given by multiplying Eq. (13.640) by two is

$$2c' = 2.07020 a_0 = 1.09550 \times 10^{-10} \text{ m} \quad (13.641)$$

The experimental bond distance from Ref. [28] and Ref. [43] is

$$20 \quad 2c' = 1.09769 \times 10^{-10} \text{ m} \quad (13.642)$$

$$2c' = 1.094 \times 10^{-10} \text{ m} \quad (13.643)$$

Substitution of Eqs. (13.639-13.640) into Eq. (11.80) is

$$b = c = 1.87628 a_0 = 9.92882 \times 10^{-11} \text{ m} \quad (13.644)$$

Substitution of Eqs. (13.639-13.640) into Eq. (11.67) is

$$25 \quad e = 0.48305 \quad (13.645)$$

Using the electron configuration of  $N_2$  (Eq. (13.620)), the radii of the  $N1s = 0.14605a_0$  (Eq. (10.51)),  $N2s = 0.69385a_0$  (Eq. (10.62)), and  $N2p = 0.78402a_0$  (Eq. (13.630)) shells and the parameters of the  $\sigma$  MO of  $N_2$  given by Eqs. (13.3-13.4), (13.639-13.641), and (13.644-13.645), the dimensional diagram and charge-density of the  $N_2$  MO are shown in Figures 19 and 20, respectively.

Despite the predictions of standard quantum mechanics that preclude the imaging of a molecular orbital, the full three-dimensional structure of the outer molecular orbital of  $N_2$  has been recently tomographically reconstructed [44]. The charge-density surface observed is consistent with that shown in Figure 20. This result constitutes direct evidence that 10 electrons are not point-particle probability waves that have no form until they are "collapsed to a point" by measurement. Rather they are physical, two-dimensional equipotential charge density surfaces.

## SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE 15 NITROGEN MOLECULE

The energies of the  $N_2$   $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. (13.639-13.640) and (13.644)) into the energy equations (Eqs. (11.207-11.212)) of  $H_2$ :

$$V_e = \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -27.70586 \text{ eV} \quad (13.646)$$

$$V_p = \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 13.14446 \text{ eV} \quad (13.647)$$

$$20 \quad T = \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 6.46470 \text{ eV} \quad (13.648)$$

$$V_m = \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -3.23235 \text{ eV} \quad (13.649)$$

$$E_T = V_e + T + V_m + V_p \quad (13.650)$$

Substitution of Eqs. (11.79) and (13.646-13.649) into Eq. (13.650) gives

$$E_T(N_2, \sigma) = \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left( \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right) = -11.32906 \text{ eV} \quad (13.651)$$

where  $E_T(N_2, \sigma)$  is the total energy of the  $\sigma$  MO of  $N_2$ . The sum,  $E_T(N_2)$ , of  $E_T(N_2, 2p)$ , the  $2p$  (AO) contribution given by Eq. (13.632), and  $E_T(N_2, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (13.651) is:

$$\begin{aligned} E_T(N_2) &= E_T(N_2, 2p) + E_T(N_2, \sigma) \\ &= -27.37174 \text{ eV} - 11.32906 \text{ eV} \\ &= -38.70080 \text{ eV} \end{aligned} \quad (13.652)$$

5

## VIBRATION OF $N_2$

The vibrational energy levels of  $N_2$  may be solved by determining the Morse potential curve from the energy relationships for the transition from two  $N$  atoms whose parameters are given by Eqs. (10.134-10.143) to the two  $N$  atoms whose parameter  $r_6$  is given by Eq. (13.630) and the  $\sigma$  MO whose parameters are given by Eqs. (13.639-13.641) and (13.644-13.645). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF THE NITROGEN MOLECULE

The equations of the radiation reaction force of nitrogen are the same as those of  $H_2$  with the substitution of the nitrogen parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{e^2}{4\pi\epsilon_0 a^3}} = 1.31794 \times 10^{16} \text{ rad/s} \quad (13.653)$$

where  $a$  is given by Eq. (13.639). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 1.31794 \times 10^{16} \text{ rad/s} = 8.67490 \text{ eV} \quad (13.654)$$

25

In Eq. (11.181), substitution of  $E_T(N_2)$  for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.654) for  $\bar{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -38.70080 \text{ eV} \sqrt{\frac{2e(8.67490 \text{ eV})}{m_e c^2}} = -0.22550 \text{ eV} \quad (13.655)$$

5 In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the  $N_2$  MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (13.655) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the  
10 vibrational energy. Using the experimental  $N_2$   $\omega_e$  of  $2358.57 \text{ cm}^{-1}$  ( $0.29243 \text{ eV}$ ) [28] for  $\bar{E}_{Kvib}$  of the transition state,  $\bar{E}_{osc}(N_2)$  is

$$\bar{E}_{osc}(N_2) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.656)$$

$$\bar{E}_{osc}(N_2) = -0.22550 \text{ eV} + \frac{1}{2} (0.29243 \text{ eV}) = -0.07929 \text{ eV} \quad (13.657)$$

## 15 TOTAL AND BOND ENERGIES OF THE NITROGEN MOLECULE

$E_{T+osc}(N_2)$ , the total energy of  $N_2$  including the Doppler term, is given by the sum of  $E_T(N_2)$  (Eq. (13.652)) and  $\bar{E}_{osc}(N_2)$  given by Eq. (13.657):

$$\begin{aligned} E_{T+osc}(N_2) &= V_e + T + V_m + V_p + E_T(N_2, 2p) + \bar{E}_{osc}(N_2) \\ &= E_T(N_2, \sigma) + E_T(N_2, 2p) + \bar{E}_{osc}(N_2) \\ &= E_T(N_2) + \bar{E}_{osc}(N_2) \end{aligned} \quad (13.658)$$

$$\begin{aligned}
E_{T+osc}(N_2) &= \left\{ \left( \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left( \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right) - 2 \sum_{n=4}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_7} \right) \right) \right. \\
&\quad \left. \left( 1 + \sqrt{\frac{\frac{e^2}{4\pi\epsilon_0 a^3}}{\frac{m_e}{m_e c^2}}} \right) + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right\} \quad (13.659) \\
&= -38.70080 \text{ eV} - 0.22550 \text{ eV} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}
\end{aligned}$$

From Eqs. (13.656-13.659), the total energy of the  $N_2$  MO is

$$\begin{aligned}
E_{T+osc}(N_2) &= -38.70080 \text{ eV} + \bar{E}_{osc}(N_2) \\
&= -38.70080 \text{ eV} - 0.22550 \text{ eV} + \frac{1}{2} (0.29243 \text{ eV}) \\
&= -38.78009 \text{ eV}
\end{aligned} \quad (13.660)$$

where the experimental  $\omega_e$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

5 The  $N_2$  bond dissociation energy,  $E_D(N_2)$ , is given by the difference in the total energies of the two  $N$  atoms and  $E_{T+osc}(N_2)$ :

$$E_D(N_2) = 2E(N) - E_{T+osc}(N_2) \quad (13.661)$$

where the energy of a nitrogen atom is [6]

$$E(N) = -14.53414 \text{ eV} \quad (13.662)$$

10 Thus, the  $N_2$  bond dissociation energy,  $E_D(N_2)$ , given by Eqs. (13.660-13.662) is

$$\begin{aligned}
E_D(N_2) &= -2(14.53414 \text{ eV}) - E_{T+osc}(N_2) \\
&= -29.06828 \text{ eV} - (-38.78009 \text{ eV}) \\
&= 9.71181 \text{ eV}
\end{aligned} \quad (13.663)$$

The experimental  $N_2$  bond dissociation energy from Ref. [43] and Ref. [45] is

$$E_D(N_2) = 9.756 \text{ eV} \quad (13.664)$$

$$E_D(N_2) = 9.764 \text{ eV} \quad (13.665)$$

15 The results of the determination of bond parameters of  $N_2$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations

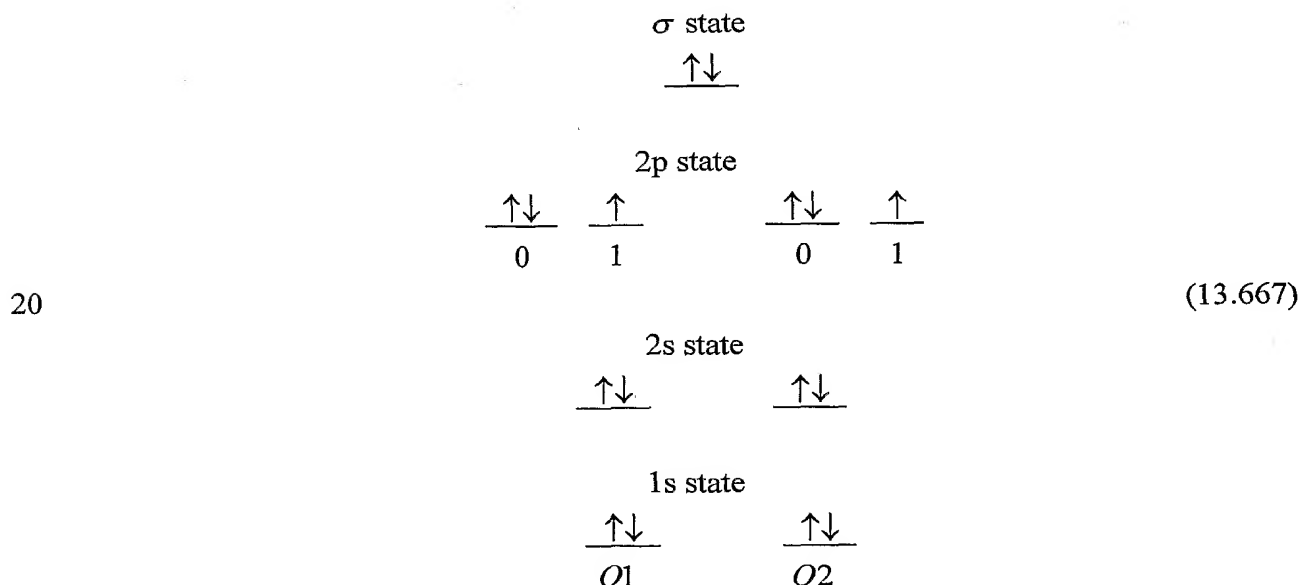
containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## OXYGEN MOLECULE

- 5 The oxygen molecule can be formed by the reaction of two oxygen atoms:



The bond in the oxygen molecule comprises a  $H_2$ -type molecular orbital (MO) with two paired electrons. The force balance equation and radius  $r_g$  of the  $2p$  shell of  $O$  is derived in the Eight-Electron Atoms section. With the formation of the  $H_2$ -type MO by the contribution of a  $2p$  electron from each  $O$  atom, a diamagnetic force arises between the remaining  $2p$  electrons and the  $H_2$ -type MO. This force from each  $O$  causes the  $H_2$ -type MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining  $2p$  electrons of each  $O$  decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of  $O_2$  is  $1s_1^2 1s_2^2 2s_1^2 2s_2^2 2p_1^3 2p_2^3 \sigma_{1,2}^2$  where the subscript designates the  $O$  atom, 1 or 2,  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is



Oxygen is predicted to be paramagnetic in agreement with observations [42].

## FORCE BALANCE OF THE $2p$ SHELL OF THE OXYGEN ATOMS OF THE OXYGEN MOLECULE

- 5 For each  $O$  atom, force balance for the outermost  $2p$  electron of  $O_2$  (electron 7) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 7 and the other  $2p$ -shell as well as the  $2s$ -shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most  $2p$  shell electron of  $O_2$
- 10 (electron 7) due to the nucleus and the inner six electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-6)e^2}{4\pi\epsilon_0 r_7^2} \mathbf{i}_r \quad (13.668)$$

- for  $r > r_6$ . The  $2p$  shell possess an external electric field given by Eq. (10.92) for  $r > r_7$ . The energy is minimized with conservation of angular momentum. This condition is met
- 15 when the magnetic forces are the same as those of the reactant oxygen atoms with  $r_7$  replacing  $r_8$ . The diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the  $p$ -orbital contributions is given by Eq. (10.156):

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3} + \frac{2}{3}\right) \frac{\hbar^2}{4m_e r_7^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{3\hbar^2}{12m_e r_7^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r \quad (13.669)$$

- And,  $\mathbf{F}_{mag\ 2}$  corresponding to the conserved spin and orbital angular momentum given by Eq.
- 20 (10.157) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{2\hbar^2}{m_e r_7^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (13.670)$$

The electric field external to the  $2p$  shell given by Eq. (10.92) for  $r > r_7$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the  $p$ -orbital electron having an electric field of +1 outside of its radius is :

$$25 \quad \mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-7}{Z-6}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_7^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (13.671)$$

The radius of the  $2p$  shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.688)) and diamagnetic (Eqs. (13.669) and (13.671)), and

paramagnetic (Eq. (13.670)) forces as follows:

$$\frac{m_e v_7^2}{r_7} = \left( \frac{(Z-6)e^2}{4\pi\epsilon_0 r_7^2} - \frac{3\hbar^2}{12m_e r_7^2 r_3} \sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_7^2 r_3} \sqrt{s(s+1)} - \left[ \frac{Z-7}{Z-6} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_7^4 m_e} 10 \sqrt{s(s+1)} \right) \quad (13.672)$$

Substitution of  $v_7 = \frac{\hbar}{m_e r_7}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.672) gives:

$$\frac{\hbar^2}{m_e r_7^3} = \frac{(Z-6)e^2}{4\pi\epsilon_0 r_7^2} - \frac{3\hbar^2}{12m_e r_7^2 r_3} \sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_7^2 r_3} \sqrt{\frac{3}{4}} - \left[ \frac{Z-7}{Z-6} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_7^4 m_e} 10 \sqrt{\frac{3}{4}} \quad (13.673)$$

5

The quadratic equation corresponding to Eq. (13.673) is

$$r_7^2 - \frac{\frac{\hbar^2}{m_e}}{\left( \frac{(Z-6)e^2}{4\pi\epsilon_0} - \left( \frac{3}{12} - \frac{2}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} r_7 - \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-7}{Z-6} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-6)e^2}{4\pi\epsilon_0} - \left( \frac{3}{12} - \frac{2}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} = 0 \quad (13.674)$$

The solution of Eq. (13.674) using the quadratic formula is:

$$r_7 = \frac{a_0 \left( (Z-6) - \left( \frac{3}{12} - \frac{2}{Z} \right) \frac{\sqrt{3}}{2r_3} \right) \pm a_0 \sqrt{\left( \frac{1}{\left( (Z-6) - \left( \frac{3}{12} - \frac{2}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)} \right)^2 + \frac{20\sqrt{3} \left[ \frac{Z-7}{Z-6} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3}{\left( (Z-6) - \left( \frac{3}{12} - \frac{2}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)}}}{2} \quad (13.675)$$

$r_3$  in units of  $a_0$

The positive root of Eq. (13.675) must be taken in order that  $r_7 > 0$ . Substitution of

$\frac{r_3}{a_0} = 0.59020$  (Eq. (10.62) with  $Z = 8$ ) into Eq. (13.675) gives

$$r_7 = 0.91088a_0 \quad (13.676)$$



## OXYGEN MOLECULE

The central forces on the  $2p$  shell of each  $O$  are increased with the formation of the  $\sigma$  MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the two  $O$  atoms at the new radius are calculated and added to the  
5 energy of the  $\sigma$  MO to give the total energy of  $O_2$ . Then, the bond energy is determined from the total  $O_2$  energy.

The radius  $r_8$  of each oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 \quad (13.677)$$

Using the initial radius  $r_8$  of each  $O$  atom and the final radius  $r_7$  of the  $O2p$  shell of  $O_2$   
10 (Eq. (13.676)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(O_2, 2p)$  of the Coulombic energy change of the  $O2p$  electrons of both atoms is determined using Eq. (10.102):

$$\begin{aligned} E_T(O_2, 2p) &= -2 \sum_{n=4}^6 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_7} - \frac{1}{r_8} \right) \\ &= -2(13.60580 \text{ eV})(0.09784)(2+3+4) \\ &= -23.96074 \text{ eV} \end{aligned} \quad (13.678)$$

15 FORCE BALANCE OF THE  $\sigma$  MO OF THE OXYGEN MOLECULE

The force balance equation for the  $\sigma$ -MO of the oxygen molecule given by Eq. (11.200) and  
Eqs. (13.633-13.634) with  $n_e = 2$  and  $|L| = \sqrt{\frac{3}{4}}\hbar$  is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left( \frac{3}{2} + \frac{\sqrt{\frac{3}{4}}}{Z} \right) \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.679)$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D - \left( \frac{1}{2} + \frac{\sqrt{\frac{3}{4}}}{Z} \right) \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.680)$$

$$20 \quad \left( \frac{5}{2} + \frac{\sqrt{\frac{3}{4}}}{Z} \right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D \quad (13.681)$$

$$a = \left( \frac{5}{2} + \frac{\sqrt{\frac{3}{4}}}{Z} \right) a_0 \quad (13.682)$$

Substitution of  $Z = 8$  into Eq. (13.682) gives

$$a = 2.60825a_0 = 1.38023 \times 10^{-10} \text{ m} \quad (13.683)$$

Substitution of Eq. (13.683) into Eq. (11.79) is

$$5 \quad c' = 1.14198a_0 = 6.04312 \times 10^{-11} \text{ m} \quad (13.684)$$

The internuclear distance given by multiplying Eq. (13.684) by two is

$$2c' = 2.28397a_0 = 1.20862 \times 10^{-10} \text{ m} \quad (13.685)$$

The experimental bond distance is [28]

$$2c' = 1.20752 \times 10^{-10} \text{ m} \quad (13.686)$$

10 Substitution of Eqs. (13.683-13.684) into Eq. (11.80) is

$$b = c = 2.34496a_0 = 1.24090 \times 10^{-10} \text{ m} \quad (13.687)$$

Substitution of Eqs. (13.683-13.684) into Eq. (11.67) is

$$e = 0.43783 \quad (13.688)$$

Using the electron configuration of  $O_2$  (Eq. (13.667)), the radii of the  $O1s = 0.12739a_0$  (Eq. 15 (10.51)),  $O2s = 0.59020a_0$  (Eq. (10.62)), and  $O2p = 0.91088a_0$  (Eq. (13.676)) shells and the parameters of the  $\sigma$  MO of  $O_2$  given by Eqs. (13.3-13.4), (13.683-13.685), and (13.687-13.688), the dimensional diagram and charge-density of the  $O_2$  MO are shown in Figures 21 and 22, respectively.

## 20 SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE OXYGEN MOLECULE

The energies of the  $O_2$   $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. (13.683-13.684) and (13.687)) into the energy equations (Eqs. (11.207-11.212)) of  $H_2$ :

$$V_e = \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -22.37716 \text{ eV} \quad (13.689)$$

$$25 \quad V_p = \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 11.91418 \text{ eV} \quad (13.690)$$

$$T = \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 4.28968 \text{ eV} \quad (13.691)$$

$$V_m = \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -2.14484 \text{ eV} \quad (13.692)$$

$$E_T = V_e + T + V_m + V_p \quad (13.693)$$

Substitution of Eqs. (11.79) and (13.689-13.692) into Eq. (13.693) gives

$$5 \quad E_T(O_2, \sigma) = \frac{-e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2}}} \left( \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right) = -8.31814 \text{ eV} \quad (13.694)$$

where  $E_T(O_2, \sigma)$  is the total energy of the  $\sigma$  MO of  $O_2$ . The sum,  $E_T(O_2)$ , of  $E_T(O_2, 2p)$ , the  $2p$  AO contribution given by Eq. (13.678), and  $E_T(O_2, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (13.694) is:

$$\begin{aligned} E_T(O_2) &= E_T(O_2, 2p) + E_T(O_2, \sigma) \\ &= -23.96074 \text{ eV} - 8.31814 \text{ eV} \\ &= -32.27888 \text{ eV} \end{aligned} \quad (13.695)$$

10

## VIBRATION OF $O_2$

The vibrational energy levels of  $O_2$  may be solved by determining the Morse potential curve from the energy relationships for the transition from two  $O$  atoms whose parameters are given by Eqs. (10.154-10.163) to the two  $O$  atoms whose parameter  $r_7$  is given by Eq. (13.676) and the  $\sigma$  MO whose parameters are given by Eqs. (13.683-13.685) and (13.687-13.688). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic 15 perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods. 20

## THE DOPPLER ENERGY TERMS OF THE OXYGEN MOLECULE

The equations of the radiation reaction force of oxygen are the same as those of  $H_2$  with the substitution of the oxygen parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$5 \quad \omega = \sqrt{\frac{e^2}{4\pi\epsilon_0 a^3}} = 9.81432 \times 10^{16} \text{ rad/s} \quad (13.696)$$

where  $a$  is given by Eq. (13.683). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = 6.45996 \text{ eV} \quad (13.697)$$

In Eq. (11.181), substitution of  $E_T(O_2)$  for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the  
 10 kinetic energy given by Eq. (13.697) for  $\bar{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -32.27888 \text{ eV} \sqrt{\frac{2e(6.45996 \text{ eV})}{m_e c^2}} = -0.16231 \text{ eV} \quad (13.698)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the  $O_2$  MO  
 15 due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (13.698) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental  $O_2$   $\omega_e$  of  $1580.19 \text{ cm}^{-1}$  ( $0.19592 \text{ eV}$ ) [28] for  $\bar{E}_{Kvib}$  of the transition state,  $\bar{E}_{osc}(O_2)$  is

$$20 \quad \bar{E}_{osc}(O_2) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.699)$$

$$\bar{E}_{osc}(O_2) = -0.16231 \text{ eV} + \frac{1}{2} (0.19592 \text{ eV}) = -0.06435 \text{ eV} \quad (13.700)$$

## TOTAL AND BOND ENERGIES OF THE OXYGEN MOLECULE

$E_{T+osc}(O_2)$ , the total energy of  $O_2$  including the Doppler term, is given by the sum of  
 25  $E_T(O_2)$  (Eq. (13.695)) and  $\bar{E}_{osc}(O_2)$  given by Eq. (13.700):

$$\begin{aligned}
E_{T+osc}(O_2) &= V_e + T + V_m + V_p + E_T(O_2, 2p) + \bar{E}_{osc}(O_2) \\
&= E_T(O_2, \sigma) + E_T(O_2, 2p) + \bar{E}_{osc}(O_2) \\
&= E_T(O_2) + \bar{E}_{osc}(O_2)
\end{aligned} \tag{13.701}$$

$$\begin{aligned}
E_{T+osc}(O_2) &= \left\{ \left( \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right) - 2 \sum_{n=4}^6 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_7} - \frac{1}{r_8} \right) \right\} \\
&\quad \left\{ \left( 1 + \sqrt{\frac{2\hbar\sqrt{\frac{e^2}{4\pi\epsilon_0 a^3}}}}{m_e c^2} \right) + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right\} \\
&= -32.27888 \text{ eV} - 0.16231 \text{ eV} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}
\end{aligned} \tag{13.702}$$

From Eqs. (13.699-13.702), the total energy of the  $O_2$  MO is

$$\begin{aligned}
E_{T+osc}(O_2) &= -32.27888 \text{ eV} + \bar{E}_{osc}(O_2) \\
&= -32.27888 \text{ eV} - 0.16231 \text{ eV} + \frac{1}{2} (0.19592 \text{ eV}) \\
&= -32.34323 \text{ eV}
\end{aligned} \tag{13.703}$$

5 where the experimental  $\omega_e$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

The  $O_2$  bond dissociation energy,  $E_D(O_2)$ , is given by the difference in the total energies of the two  $O$  atoms and  $E_{T+osc}(O_2)$ :

$$E_D(O_2) = 2E(O) - E_{T+osc}(O_2) \tag{13.704}$$

where the energy of an oxygen atom is [6]

$$10 \quad E(O) = -13.61806 \text{ eV} \tag{13.705}$$

Thus, the  $O_2$  bond dissociation energy,  $E_D(O_2)$ , given by Eqs. (13.703-13.705) is

$$\begin{aligned}
E_D(O_2) &= -2(13.61806 \text{ eV}) - E_{T+osc}(O_2) \\
&= -27.23612 \text{ eV} - (-32.34323 \text{ eV}) \\
&= 5.10711 \text{ eV}
\end{aligned} \tag{13.706}$$

The experimental  $O_2$  bond dissociation energy from Ref. [46] and Ref. [47] is

$$E_D(O_2) = 5.11665 \text{ eV} \tag{13.707}$$

$$15 \quad E_D(O_2) = 5.116696 \text{ eV} \tag{13.708}$$

The results of the determination of bond parameters of  $O_2$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

5

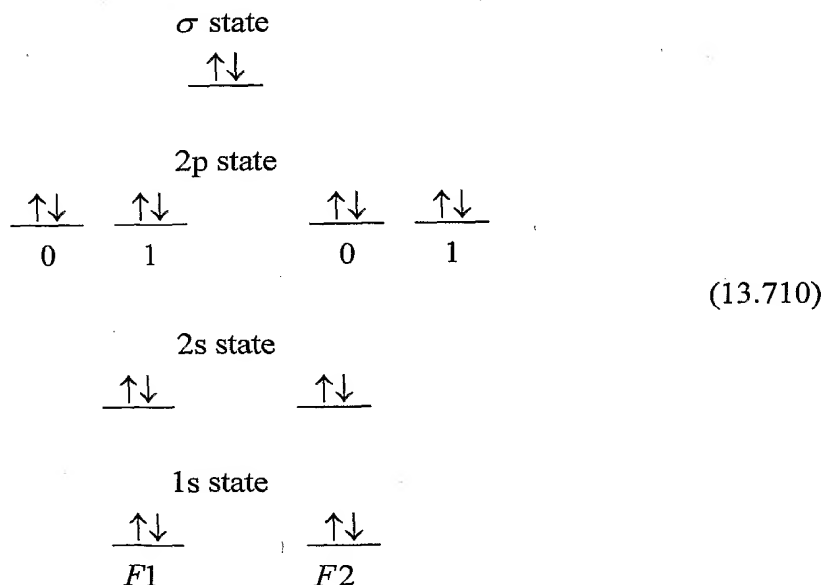
## FLUORINE MOLECULE

The fluorine molecule can be formed by the reaction of two fluorine atoms:



The bond in the fluorine molecule comprises a  $H_2$ -type molecular orbital (MO) with two  
 10 paired electrons. The force balance equation and radius  $r_0$  of the  $2p$  shell of  $F$  is derived in the Nine-Electron Atoms section. With the formation of the  $H_2$ -type MO by the contribution of a  $2p$  electron from each  $F$  atom, a diamagnetic force arises between the remaining  $2p$  electrons and the  $H_2$ -type MO. This force from each  $F$  causes the  $H_2$ -type MO to move to  
 15 greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining  $2p$  electrons of each  $F$  decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of  $F_2$  is  $1s_1^2 1s_2^2 2s_1^2 2s_2^2 2p_1^4 2p_2^4 \sigma_{1,2}^2$  where the subscript designates the  $F$  atom, 1 or 2,  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is

20



Fluorine is predicted to be diamagnetic in agreement with observations [42].

## FORCE BALANCE OF THE $2p$ SHELL OF THE FLUORINE ATOMS OF 5 THE FLUORINE MOLECULE

For each  $F$  atom, force balance for the outermost  $2p$  electron of  $F_2$  (electron 8) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 8 and the other  $2p$ -shell as well as the  $2s$ -shell electrons due to spin and orbital angular momentum. The forces used are derived in the Nine-Electron  
10 Atoms section. The central Coulomb force on the outer-most  $2p$  shell electron of  $F_2$  (electron 8) due to the nucleus and the inner seven electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-7)e^2}{4\pi\epsilon_0 r_8^2} \mathbf{i}_r \quad (13.711)$$

for  $r > r_7$ . The  $2p$  shell possess an external electric field given by Eq. (10.92) for  $r > r_8$ .  
15 The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the  $p$ -orbital contributions is the same as that of the reactant fluorine atoms given by Eq. (10.176) with  $r_8$  replacing  $r_9$ :

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right) \frac{\hbar^2}{4m_e r_8^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{2\hbar^2}{12m_e r_8^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r \quad (13.712)$$

Thus,  $\mathbf{F}_{diamagnetic}$  due to the two filled  $2p$  orbitals per  $F$  atom is twice that of  $N_2$  given by  
20 Eq. (13.622) having one filled  $2p$  orbital per  $N$  atom.  $\mathbf{F}_{mag\ 2}$  corresponding to the conserved spin and orbital angular momentum is also the same as that of the reactant fluorine atoms given by Eq. (10.177) and that of  $N_2$  given by Eq. (13.623) where the outer radius of the  $2p$  shell of the  $F$  atoms of  $F_2$  is  $r_8$ .

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{3\hbar^2}{m_e r_8^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (13.713)$$

25 The electric field external to the  $2p$  shell given by Eq. (10.92) for  $r > r_8$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the  $p$ -orbital electron having an electric field of +1 outside of its radius is :

$$\mathbf{F}_{\text{diamagnetic } 2} = -\left[\frac{Z-8}{Z-7}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_8^4}10\sqrt{s(s+1)}\mathbf{i}_r \quad (13.714)$$

In addition, the contribution of a  $2p$  electron from each  $F$  atom in the formation of the  $\sigma$  MO gives rise to a paramagnetic force on the remaining paired  $2p$  electrons. The force  $\mathbf{F}_{\text{mag } 3}$  is given by Eq. (13.625) wherein the radius is  $r_8$ :

$$5 \quad \mathbf{F}_{\text{mag } 3} = \frac{\hbar^2}{4m_e r_8^3}\sqrt{s(s+1)}\mathbf{i}_r \quad (13.715)$$

The radius of the  $2p$  shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.711)) and diamagnetic (Eqs. (13.712) and (13.714)), and paramagnetic (Eqs. (13.713) and (13.715)) forces as follows:

$$\frac{m_e v_8^2}{r_8} = \left( \frac{(Z-7)e^2}{4\pi\epsilon_0 r_8^2} - \frac{2\hbar^2}{12m_e r_8^2 r_3} \sqrt{s(s+1)} + \frac{3\hbar^2}{Zm_e r_8^2 r_3} \sqrt{s(s+1)} - \left[ \frac{Z-8}{Z-7} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_8^4 m_e} 10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_8^3} \sqrt{s(s+1)} \right) \quad (13.716)$$

10 Substitution of  $v_8 = \frac{\hbar}{m_e r_8}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.716) gives:

$$\frac{\hbar^2}{m_e r_8^3} - \frac{\hbar^2}{4m_e r_8^3} \sqrt{\frac{3}{4}} = \frac{(Z-7)e^2}{4\pi\epsilon_0 r_8^2} - \frac{2\hbar^2}{12m_e r_8^2 r_3} \sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Zm_e r_8^2 r_3} \sqrt{\frac{3}{4}} - \left[ \frac{Z-8}{Z-7} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_8^4 m_e} 10\sqrt{\frac{3}{4}} \quad (13.717)$$

The quadratic equation corresponding to Eq. (13.717) is

$$r_8^2 - \frac{\frac{\hbar^2}{m_e} \left( 1 - \frac{\sqrt{3}}{8} \right)}{\left( \frac{(Z-7)e^2}{4\pi\epsilon_0} - \left( \frac{2}{12} - \frac{3}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} r_8 - \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-8}{Z-7} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10\sqrt{\frac{3}{4}}}{\left( \frac{(Z-7)e^2}{4\pi\epsilon_0} - \left( \frac{2}{12} - \frac{3}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} = 0$$

$$15 \quad (13.718)$$

The solution of Eq. (13.718) using the quadratic formula is:



$$r_8 = \frac{a_0 \left(1 - \frac{\sqrt{3}}{8}\right)}{\left((Z-7) - \left(\frac{2}{12} - \frac{3}{Z}\right) \frac{\sqrt{3}}{2r_3}\right)} \pm a_0 \sqrt{\frac{241}{\left(\frac{1 - \frac{\sqrt{3}}{8}}{\left((Z-7) - \left(\frac{2}{12} - \frac{3}{Z}\right) \frac{\sqrt{3}}{2r_3}\right)}\right)^2 + \frac{20\sqrt{3} \left[\frac{Z-8}{Z-7}\right] \left(1 - \frac{\sqrt{2}}{2}\right) r_3}{\left((Z-7) - \left(\frac{2}{12} - \frac{3}{Z}\right) \frac{\sqrt{3}}{2r_3}\right)}}} \quad (13.719)$$

$r_3$  in units of  $a_0$

The positive root of Eq. (13.719) must be taken in order that  $r_8 > 0$ . Substitution of

$\frac{r_3}{a_0} = 0.51382$  (Eq. (10.62) with  $Z = 9$ ) into Eq. (13.719) gives

$$r_8 = 0.73318a_0 \quad (13.720)$$

5

## ENERGIES OF THE $2p$ SHELL OF THE FLUORINE ATOMS OF THE FLUORINE MOLECULE

The central forces on the  $2p$  shell of each  $F$  are increased with the formation of the  $\sigma$  MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms  
10 of the total energy of the two  $F$  atoms at the new radius are calculated and added to the energy of the  $\sigma$  MO to give the total energy of  $F_2$ . Then, the bond energy is determined from the total  $F_2$  energy.

The radius  $r_9$  of each fluorine atom before bonding is given by Eq. (10.182):

$$r_9 = 0.78069a_0 \quad (13.721)$$

15 Using the initial radius  $r_9$  of each  $F$  atom and the final radius  $r_8$  of the  $F2p$  shell of  $F_2$  (Eq. (13.720)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(F_2, 2p)$  of the Coulombic energy change of the  $F2p$  electrons of both atoms is determined using Eq. (10.102):

$$\begin{aligned} E_T(F_2, 2p) &= -2 \sum_{n=4}^7 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_8} - \frac{1}{r_9} \right) \\ &= -2(13.60580 \text{ eV})(0.08301)(2+3+4+5) \\ &= -31.62353 \text{ eV} \end{aligned} \quad (13.722)$$

# FORCE BALANCE OF THE $\sigma$ MO OF THE FLUORINE MOLECULE

The relativistic diamagnetic force  $\mathbf{F}_{\text{diamagneticMO}_2}$  of  $F_2$  is one half that of  $N_2$  due to the two versus one filled  $2p$  orbitals per atom at the focus. The force balance equation for the  $\sigma$ -  
5 MO of the fluorine molecule is given by Eq. (11.200) and Eqs. (13.633-13.634) with the correction of 1/2 due the two  $2p$  orbitals per  $F$  after Eqs. (10.2-10.11),  $n_e = 2$ , and  $|L| = \hbar$ :

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(\frac{5}{2} + \frac{1}{2Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.723)$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D - \left(\frac{3}{2} + \frac{1}{2Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.724)$$

$$\left(\frac{7}{2} + \frac{1}{2Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D \quad (13.725)$$

$$10 \quad a = \left(\frac{7}{2} + \frac{1}{2Z}\right) a_0 \quad (13.726)$$

Substitution of  $Z = 9$  into Eq. (13.726) gives

$$a = 3.55556a_0 = 1.88152 \times 10^{-10} \text{ m} \quad (13.727)$$

Substitution of Eq. (13.727) into Eq. (11.79) is

$$c' = 1.33333a_0 = 7.05569 \times 10^{-11} \text{ m} \quad (13.728)$$

15 The internuclear distance given by multiplying Eq. (13.728) by two is

$$2c' = 2.66667a_0 = 1.41114 \times 10^{-10} \text{ m} \quad (13.729)$$

The experimental bond distance is [28]

$$2c' = 1.41193 \times 10^{-10} \text{ m} \quad (13.730)$$

Substitution of Eqs. (13.727-13.728) into Eq. (11.80) is

$$20 \quad b = c = 3.29609a_0 = 1.74421 \times 10^{-10} \text{ m} \quad (13.731)$$

Substitution of Eqs. (13.727-13.728) into Eq. (11.67) is

$$e = 0.37500 \quad (13.732)$$

Using the electron configuration of  $F_2$  (Eq. (13.710)), the radii of the  $F1s = 0.11297a_0$  (Eq. (10.51)),  $F2s = 0.51382a_0$  (Eq. (10.62)), and  $F2p = 0.73318a_0$  (Eq. (13.720)) shells and the  
25 parameters of the  $\sigma$  MO of  $F_2$  given by Eqs. (13.3-13.4), (13.727-13.728), and (13.731-13.732), the dimensional diagram and charge-density of the  $F_2$  MO are shown in Figures 23 and 24, respectively.

## SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE FLUORINE MOLECULE

- 5 The energies of the  $F_2$   $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. (13.683-13.684) and (13.687)) into the energy equations (Eqs. (11.207-11.212)) of  $H_2$ :

$$V_e = \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.09139 \text{ eV} \quad (13.733)$$

$$V_p = \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 10.20435 \text{ eV} \quad (13.734)$$

$$T = \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 2.26285 \text{ eV} \quad (13.735)$$

$$10 \quad V_m = \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -1.13143 \text{ eV} \quad (13.736)$$

$$E_T = V_e + T + V_m + V_p \quad (13.737)$$

Substitution of Eqs. (11.79) and (13.733-13.736) into Eq. (13.737) gives

$$E_T(F_2, \sigma) = \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left( \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right) = -4.75562 \text{ eV} \quad (13.738)$$

- where  $E_T(F_2, \sigma)$  is the total energy of the  $\sigma$  MO of  $F_2$ . The sum,  $E_T(F_2)$ , of  $E_T(F_2, 2p)$ ,  
 15 the  $2p$  AO contribution given by Eq. (13.722), and  $E_T(F_2, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (13.738) is:

$$\begin{aligned} E_T(F_2) &= E_T(F_2, 2p) + E_T(F_2, \sigma) \\ &= -31.62353 \text{ eV} - 4.75562 \text{ eV} \\ &= -36.37915 \text{ eV} \end{aligned} \quad (13.739)$$

## VIBRATION OF $F_2$

- 20 The vibrational energy levels of  $F_2$  may be solved by determining the Morse potential curve from the energy relationships for the transition from two  $F$  atoms whose parameters are given by Eqs. (10.174-10.183) to the two  $F$  atoms whose parameter  $r_8$  is given by Eq.

(13.720) and the  $\sigma$  MO whose parameters are given by Eqs. (13.727-13.729) and (13.731-13.732). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter  
 5 (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

#### THE DOPPLER ENERGY TERMS OF THE FLUORINE MOLECULE

10 The equations of the radiation reaction force of fluorine are the same as those of  $H_2$  with the substitution of the fluorine parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{e^2}{4\pi\epsilon_0 a^3}} = 6.16629 \times 10^{15} \text{ rad/s} \quad (13.740)$$

where  $a$  is given by Eq. (13.727). The kinetic energy,  $E_K$ , is given by Planck's equation

15 (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 6.16629 \times 10^{15} \text{ rad/s} = 4.05876 \text{ eV} \quad (13.741)$$

In Eq. (11.181), substitution of  $E_T(F_2)$  for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.741) for  $\bar{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

$$20 \quad \bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -36.37915 \text{ eV} \sqrt{\frac{2e(4.05876 \text{ eV})}{m_e c^2}} = -0.14499 \text{ eV} \quad (13.742)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the  $F_2$  MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given  
 25 by Eq. (13.742) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental  $F_2$   $\omega_e$  of  $916.64 \text{ cm}^{-1}$  ( $0.11365 \text{ eV}$ ) [28] for  $\bar{E}_{Kvib}$  of the transition state,  $\bar{E}_{osc}(F_2)$  is

$$\bar{E}_{osc}(F_2) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.743)$$

$$\bar{E}_{osc}(F_2) = -0.14499 \text{ eV} + \frac{1}{2} (0.11365 \text{ eV}) = -0.08817 \text{ eV} \quad (13.744)$$

### TOTAL AND BOND ENERGIES OF THE FLUORINE MOLECULE

- 5  $E_{T+osc}(F_2)$ , the total energy of  $F_2$  including the Doppler term, is given by the sum of  $E_T(F_2)$  (Eq. (13.739)) and  $\bar{E}_{osc}(F_2)$  given by Eq. (13.744):

$$\begin{aligned} E_{T+osc}(F_2) &= V_e + T + V_m + V_p + E_T(F_2, 2p) + \bar{E}_{osc}(F_2) \\ &= E_T(F_2, \sigma) + E_T(F_2, 2p) + \bar{E}_{osc}(F_2) \\ &= E_T(F_2) + \bar{E}_{osc}(F_2) \end{aligned} \quad (13.745)$$

$$\begin{aligned} E_{T+osc}(F_2) &= \left\{ \left( \frac{-e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2}}} \left( \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right) - 2 \sum_{n=4}^7 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_8} - \frac{1}{r_9} \right) \right) \right. \\ &\quad \left. \left( 1 + \sqrt{\frac{\frac{e^2}{4\pi\epsilon_0 a^3}}{\frac{m_e}{m_e c^2}}} \right) + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right\} \quad (13.746) \\ &= -36.37915 \text{ eV} - 0.14499 \text{ eV} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \end{aligned}$$

From Eqs. (13.743-13.746), the total energy of the  $F_2$  MO is

$$\begin{aligned} E_{T+osc}(F_2) &= -36.37915 \text{ eV} + \bar{E}_{osc}(F_2) \\ 10 \quad &= -36.37915 \text{ eV} - 0.14499 \text{ eV} + \frac{1}{2} (0.11365 \text{ eV}) \\ &= -36.46732 \text{ eV} \end{aligned} \quad (13.747)$$

where the experimental  $\omega_e$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

The  $F_2$  bond dissociation energy,  $E_D(F_2)$ , is given by the difference in the total energies of the two  $F$  atoms and  $E_{T+osc}(F_2)$ :

$$E_D(F_2) = 2E(F) - E_{T+osc}(F_2) \quad (13.748)$$

- 15 where the energy of a fluorine atom is [6]

$$E(F) = -17.42282 \text{ eV} \quad (13.749)$$

Thus, the  $F_2$  bond dissociation energy,  $E_D(F_2)$ , given by Eqs. (13.747-13.749) is

$$\begin{aligned} E_D(F_2) &= -2(17.42282 \text{ eV}) - E_{T+osc}(F_2) \\ &= -34.84564 \text{ eV} - (-36.46732 \text{ eV}) \\ &= 1.62168 \text{ eV} \end{aligned} \quad (13.750)$$

The experimental  $F_2$  bond dissociation energy is [48]

$$5 \quad E_D(F_2) = 1.606 \text{ eV} \quad (13.751)$$

The results of the determination of bond parameters of  $F_2$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

10

## CHLORINE MOLECULE

The chlorine molecule can be formed by the reaction of two chlorine atoms:



The chlorine molecule can be solved by using the hybridization approach used to solve the methane series  $CH_{n=1,2,3,4}$ . In the methane series, the  $2s$  and  $2p$  shells of carbon hybridize to form a single  $2sp^3$  shell to achieve an energy minimum, and in a likewise manner, the  $3s$  and  $3p$  shells of chlorine hybridize to form a single  $3sp^3$  shell which forms the bonding orbital of  $Cl_2$ .

## 20 FORCE BALANCE OF $Cl_2$

$Cl_2$  has two spin-paired electrons in a chemical bond between the chlorine atoms. The  $Cl_2$  molecular orbital (MO) is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal  $H_2$  MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, each  $Cl$  atom could contribute a  $3p$  electron to form a  $\sigma$  MO ( $H_2$ -type ellipsoidal MO) as in the case of  $N_2$ ,  $O_2$ , and  $F_2$ . However, such a bond is not possible with the outer  $Cl$  electrons in their ground state since the resulting  $3p$  shells of chlorine atoms would overlap which is not energetically stable. Thus, when bonding, the chlorine  $3s$  and  $3p$  shells

hybridize to form a single  $3sp^3$  shell to achieve an energy minimum.

The *Cl* electron configuration given in the Seventeen-Electron Atoms section is  $1s^2 2s^2 2p^6 3s^2 3p^5$ , and the orbital arrangement is

$$\begin{array}{ccc} & \text{3p state} & \\ \uparrow \downarrow & \uparrow \downarrow & \uparrow \\ \hline 1 & 0 & -1 \end{array} \quad (13.753)$$

5 corresponding to the ground state  $^2P_{3/2}^0$ . The radius  $r_{17}$  of the  $3p$  shell given by Eq. (10.363) is

$$r_{17} = 1.05158a_0 \quad (13.754)$$

The energy of the chlorine  $3p$  shell is the negative of the ionization energy of the chlorine atom given by Eq. (10.364). Experimentally, the energy is [6]

$$10 \quad E(3p \text{ shell}) = -E(\text{ionization}; Cl) = -12.96764 \text{ eV} \quad (13.755)$$

The *Cl* $3s$  atomic orbital (AO) combines with the *Cl* $3p$  AOs to form a single  $3sp^3$  hybridized orbital (HO) with the orbital arrangement

$$\begin{array}{cccc} & \text{2sp}^3 \text{ state} & & \\ \uparrow \downarrow & \uparrow \downarrow & \uparrow \downarrow & \uparrow \\ \hline 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \quad (13.756)$$

where the quantum numbers  $(\ell, m_\ell)$  are below each electron. The total energy of the state is  
 15 given by the sum over the seven electrons. Using only the largest-force terms of the outer most and next inner shell, the calculated energies for the chlorine atom and the ions: *Cl*, *Cl*<sup>+</sup>, *Cl*<sup>2+</sup>, *Cl*<sup>3+</sup>, *Cl*<sup>4+</sup>, *Cl*<sup>5+</sup> and *Cl*<sup>6+</sup> are given in Eqs. (10.363-10.364), (10.353-10.354), (10.331-10.332), (10.309-10.310), (10.288-10.289), (10.255-10.256), and (10.235-10.236), respectively. The sum  $E_T(Cl, 3sp^3)$  of the experimental energies of *Cl* and these ions is [6]

$$\begin{aligned} 20 \quad E_T(Cl, 3sp^3) &= \left( \begin{array}{l} 12.96764 \text{ eV} + 23.814 \text{ eV} + 39.61 \text{ eV} + 53.4652 \text{ eV} \\ + 67.8 \text{ eV} + 97.03 \text{ eV} + 114.1958 \text{ eV} \end{array} \right) \\ &= 408.88264 \text{ eV} \end{aligned} \quad (13.757)$$

The spin and orbital-angular-momentum interactions cancel such that the energy of the  $E_T(Cl, 3sp^3)$  is purely Coulombic. By considering that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{3sp^3}$  of the *Cl* $3sp^3$  shell may be calculated from the Coulombic energy using Eq. (10.102):

$$r_{3sp^3} = \sum_{n=10}^{16} \frac{(Z-n)e^2}{8\pi\epsilon_0 (e408.8826 \text{ eV})} = \frac{248}{8\pi\epsilon_0 (e408.8826 \text{ eV})} = 0.93172a_0 \quad (13.758)$$

where  $Z = 17$ . Using Eqs. (10.102) and (13.758), the Coulombic energy  $E_{Coulomb}(Cl, 3sp^3)$  of the outer electron of the  $Cl3sp^3$  shell is

$$E_{Coulomb}(Cl, 3sp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{3sp^3}} = \frac{-e^2}{8\pi\epsilon_0 0.93172a_0} = -14.60295 \text{ eV} \quad (13.759)$$

5 The calculated energy of the  $C2sp^3$  shell of  $14.63489 \text{ eV}$  given by Eq. (13.428), and nitrogen's calculated energy of  $14.61664 \text{ eV}$  given by Eq. (10.143) is a close match with  $E_{Coulomb}(Cl, 3sp^3)$ .

The unpaired  $Cl3sp^3$  electron from each of two chlorine atoms combine to form a molecular orbital. The nuclei of the  $Cl$  atoms are along the internuclear axis and serve as the  
10 foci. Due to symmetry, the other  $Cl$  electrons are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix IV.) Thus, the energies in the  $Cl$  MO involve only the two  $Cl3sp^3$  electrons. The forces are determined by these energies.

As in the case of  $H_2$ , the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $Cl3sp^3$  HO for distances shorter than the radius of  
15 the  $Cl3sp^3$  shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the nuclei and is continuous with the  $Cl3sp^3$  shell at each  $Cl$  atom. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the  $Cl3sp^3$  shell. As in the case with  $OH$ ,  $NH$ , and  $CH$  (where the latter also demonstrates  $sp^3$  hybridization) the linear combination of the  $H_2$ -type ellipsoidal MO with each  $Cl3sp^3$  HO must involve a 25% contribution from  
20 the  $H_2$ -type ellipsoidal MO to the  $Cl3sp^3$  HO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $Cl_2$  MO must comprise two  $Cl3sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the two  $Cl3sp^3$  HOs:





The force balance of the  $Cl_2$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.760) and the energy matching condition between the  $H_2$ -type-ellipsoidal-MO and  $Cl3sp^3$ -HO components of the MO.

As in the case with  $OH$  (Eq. (13.57)),  $NH$  (Eq. (13.247)), and  $CH$  (Eq. 13.429)), the  $H_2$ -  
 5 type ellipsoidal MO comprises 75% of the  $Cl_2$  MO; so, the electron charge density in Eq. (11.65) is given by  $-0.75e$ . Since the chlorine atoms of  $Cl_2$  are hybridized and the  $k$  parameter is different from unity in order to meet the boundary constraints, both  $k$  and  $k'$  must comprise the corresponding hybridization factors. (In contrast, the chlorine atom of a  $C-Cl$  bond of an alkyl chloride is not hybridized, and only  $k'$  must comprise the  
 10 corresponding hybridization factor.) The force constant  $k'$  to determine the ellipsoidal parameter  $c'$  in terms of the central force of the foci is given by Eq. (13.59), except that  $k'$  is divided by two since the  $H_2$ -type-ellipsoidal-MO is physically divided between two  $Cl3sp^3$  HOs. In addition, the energy matching at both  $Cl3sp^3$  HOs further requires that  $k'$  be corrected the hybridization factor given by Eq. (13.762). Thus,  $k'$  of the  $H_2$ -type-  
 15 ellipsoidal-MO component of the  $Cl_2$  MO is

$$k' = C_{Cl3sp^3HO} \frac{(0.75)}{2} \frac{2e^2}{4\pi\epsilon_0} = 0.93172 \frac{(0.75)}{2} \frac{2e^2}{4\pi\epsilon_0} \quad (13.761)$$

The distance from the origin to each focus  $c'$  is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal  $Cl-Cl$ -bond  $b=c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq.  
 20 (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of the  $Cl_2$  MO. Since the  $Cl_2$  MO comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $Cl3sp^3$  HOs at each end of the molecule, the energy  $E(Cl,3sp^3)$  in Eq. (13.759) adds to that of the  $H_2$ -type ellipsoidal MO to give the total energy of the  $Cl_2$  MO. From the energy equation and the relationship between the axes,  
 25 the dimensions of the  $Cl_2$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ ,  $T$ , and  $V_m$  are those of  $H_2$  (Eqs. (11.207-11.211)) except that they are corrected for electron hybridization. Hybridization gives rise to the  $Cl3sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(Cl,3sp^3)$  given by Eq. (13.759). To meet the

equipotential condition of the union of the  $H_2$ -type-ellipsoidal-MO with each  $Cl3sp^3$  HO, the electron energies are normalized by the ratio of  $14.60295 \text{ eV}$ , the magnitude of  $E_{Coulomb}(Cl, 3sp^3)$  given by Eq. (13.759), and  $13.605804 \text{ eV}$ , the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). This  
 5 normalizes the energies to match that of the Coulombic energy alone to meet the energy matching condition of the  $Cl_2$  MO under the influence of the two  $Cl3sp^3$  HOs bridged by the  $H_2$ -type-ellipsoidal MO. The hybridization energy factor  $C_{Cl3sp^3 HO}$  is

$$C_{Cl3sp^3 HO} = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{3sp^3}}} = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 0.93172 a_0}} = \frac{13.605804 \text{ eV}}{14.60295 \text{ eV}} = 0.93172 \quad (13.762)$$

The total energy  $E_T(Cl_2)$  of the  $Cl_2$  MO is given by the sum of the energies of the orbitals,  
 10 the  $H_2$ -type ellipsoidal MO and the two  $Cl3sp^3$  HOs, that form the hybridized  $Cl_2$  MO.  $E_T(Cl_2)$  follows from by Eq. (13.74) for  $OH$ , but the energy of the  $Cl3sp^3$  HO given by Eq. (13.759) is substituted for the energy of  $O$  and the  $H_2$ -type-ellipsoidal-MO energies are those of  $H_2$  (Eqs. (11.207-11.212)) multiplied by the electron hybridization factor rather than by the factor of 0.75:

$$E_T(Cl_2) = E_T + E_{Coulomb}(Cl, 3sp^3) \\
 15 \quad = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.93172) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.60295 \text{ eV} \quad (13.763)$$

To match the boundary condition that the total energy of the entire the  $H_2$ -type ellipsoidal MO is given by Eqs. (11.212) and (13.75),  $E_T(Cl_2)$  given by Eq. (13.763) is set equal to Eq. (13.75):

$$E_T(Cl_2) = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.93172) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.60295 \text{ eV} = -31.63537 \text{ eV} \\
 20 \quad (13.764)$$

From the energy relationship given by Eq. (13.764) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $Cl_2$  MO can be solved.

Substitution of Eqs. (13.60) and (13.761) into Eq. (13.764) gives

$$\frac{e^2}{8\pi\epsilon_0\sqrt{\frac{4aa_0}{3(0.93172)}}} \left[ (0.93172) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{4aa_0}{3(0.93172)}}}{a - \sqrt{\frac{4aa_0}{3(0.93172)}}} - 1 \right] = e17.03242$$

(13.765)

The most convenient way to solve Eq. (13.765) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$5 \quad a = 2.46500a_0 = 1.30442 \times 10^{-10} \text{ m} \quad (13.766)$$

Substitution of Eq. (13.766) into Eq. (13.60) gives

$$c' = 1.87817a_0 = 9.93887 \times 10^{-11} \text{ m} \quad (13.767)$$

The internuclear distance given by multiplying Eq. (13.767) by two is

$$2c' = 3.75635a_0 = 1.98777 \times 10^{-10} \text{ m} \quad (13.768)$$

10 The experimental bond distance is [28]

$$2c' = 1.988 \times 10^{-10} \text{ m} \quad (13.769)$$

Substitution of Eqs. (13.766-13.767) into Eq. (13.62) gives

$$b = c = 1.59646a_0 = 8.44810 \times 10^{-11} \text{ m} \quad (13.770)$$

Substitution of Eqs. (13.766-13.767) into Eq. (13.63) gives

$$15 \quad e = 0.76194 \quad (13.771)$$

The *Cl* nuclei comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $Cl3sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{3sp^3} = 0.93172a_0$  is the radius of the  $Cl3sp^3$  shell. Substitution of Eqs. (13.766-13.767)

20 into Eq. (13.261) gives

$$\theta' = 81.72^\circ \quad (13.772)$$

Then, the angle  $\theta_{Cl3sp^3HO}$  the radial vector of the  $Cl3sp^3$  HO makes with the internuclear axis is

$$\theta_{Cl3sp^3HO} = 180^\circ - 81.72^\circ = 98.28^\circ \quad (13.773)$$

25 as shown in Figure 25. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{H_2MO}$

between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $Cl3sp^3$  radial vector obeys the following relationship:

$$r_{3sp^3} \sin \theta_{Cl3sp^3HO} = 0.93172a_0 \sin \theta_{Cl3sp^3HO} = b \sin \theta_{H_2MO} \quad (13.774)$$

such that

$$5 \quad \theta_{H_2MO} = \sin^{-1} \frac{0.93172a_0 \sin \theta_{Cl3sp^3HO}}{b} = \sin^{-1} \frac{0.93172a_0 \sin 98.28^\circ}{b} \quad (13.775)$$

with the use of Eq. (13.773). Substitution of Eq. (13.770) into Eq. (13.775) gives

$$\theta_{H_2MO} = 35.28^\circ \quad (13.776)$$

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$10 \quad d_{H_2MO} = a \cos \theta_{H_2MO} \quad (13.777)$$

Substitution of Eqs. (13.766) and (13.776) into Eq. (13.777) gives

$$d_{H_2MO} = 2.01235a_0 = 1.06489 \times 10^{-10} \text{ m} \quad (13.778)$$

The distance  $d_{Cl3sp^3HO}$  along the internuclear axis from the origin of each  $Cl$  atom to the point of intersection of the orbitals is given by

$$15 \quad d_{Cl3sp^3HO} = d_{H_2MO} - c' \quad (13.779)$$

Substitution of Eqs. (13.768) and (13.778) into Eq. (13.779) gives

$$d_{Cl3sp^3HO} = 0.13417a_0 = 7.10022 \times 10^{-12} \text{ m} \quad (13.780)$$

As shown in Eq. (13.760), a factor of 0.25 of the charge-density of the  $H_2$ -type ellipsoidal MO is distributed on each  $Cl3sp^3$  HO. Using the orbital composition of  $Cl_2$  (Eq. (13.760)), the radii of the  $Cl1s = 0.05932a_0$  (Eq. (10.51)),  $Cl2s = 0.25344a_0$  (Eq. (10.62)),  $Cl2p = 0.31190a_0$  (Eq. (10.212)), and  $Cl3sp^3 = 0.93172a_0$  (Eq. (13.758)) shells, and the parameters of the  $Cl_2$  MO given by Eqs. (13.3-13.4), (13.766-13.768), and (13.770-13.771), the dimensional diagram and charge-density of the  $Cl_2$  MO comprising the linear combination of the  $H_2$ -type ellipsoidal MO and two  $Cl3sp^3$  HOs according to Eq. (13.760) are shown in Figures 25 and 26, respectively.

## ENERGIES OF $Cl_2$

The energies of  $Cl_2$  are given by the substitution of the semiprincipal axes (Eqs. (13.766-13.767) and (13.770)) into the energy equations, (Eq. (13.763) and Eqs. (11.207-11.211) of 5  $H_2$ ) that are corrected for electron hybridization using Eq. (13.762):

$$V_e = (0.93172) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -27.02007 \text{ eV} \quad (13.781)$$

$$V_p = \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 7.24416 \text{ eV} \quad (13.782)$$

$$T = (0.93172) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 5.48074 \text{ eV} \quad (13.783)$$

$$V_m = (0.93172) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -2.74037 \text{ eV} \quad (13.784)$$

$$10 \quad E_T(^{35}Cl_2) = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.93172) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.60295 \text{ eV} = -31.63849 \text{ eV} \quad (13.785)$$

where  $E_T(Cl_2)$  is given by Eq. (13.763) which is reiteratively matched to Eq. (13.75) within five-significant-figure round-off error.

## 15 VIBRATION AND ROTATION OF $Cl_2$

In  $Cl_2$ , the division of the  $H_2$ -type ellipsoidal MO between the two  $Cl3sp^3$  HOs and the hybridization must be considered in determining the vibrational parameters. One approach is to use Eq. (13.761) for the force constant and  $r_{3sp^3}$  given by Eq. (13.758) for the distance parameter of the central force in Eq. (11.213) since the  $H_2$ -type ellipsoidal MO is energy 20 matched to the  $Cl3sp^3$  HOs. With the substitution of the  $Cl_2$  parameters in Eqs. (11.213-11.217), the angular frequency of the oscillation is

$$\begin{aligned}
 \omega &= \sqrt{\frac{254}{\mu} \left[ \frac{0.93172 (0.75)}{2} \frac{e^2}{8\pi\epsilon_0 (r_{3sp^3})^3} - \frac{e^2}{8\pi\epsilon_0 (r_{3sp^3} + c')^3} \right]} \\
 &= \sqrt{\frac{0.93172 (0.75)}{2} \frac{e^2}{8\pi\epsilon_0 (0.93172)^3} - \frac{e^2}{8\pi\epsilon_0 (0.93172a_0 + 1.87817a_0)^3}} \\
 &\quad \frac{35}{2} m_p \\
 &= 1.01438 \times 10^{14} \text{ rad/s}
 \end{aligned} \tag{13.786}$$

where  $c'$  is given by Eq. (13.767), and the reduced mass of  $^{35}\text{Cl}_2$  is given by:

$$\mu_{^{35}\text{Cl}_2} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(35)(35)}{35 + 35} m_p \tag{13.787}$$

where  $m_p$  is the proton mass. Thus, during bond formation, the perturbation of the orbit  
 5 determined by an inverse-squared force results in simple harmonic oscillatory motion of the  
 orbit, and the corresponding frequency,  $\omega(0)$ , for  $^{35}\text{Cl}_2$  given by Eqs. (11.136), (11.148),  
 and (13.786) is

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{301.19 \text{ Nm}^{-1}}{\mu}} = 1.01438 \times 10^{14} \text{ radians/s} \tag{13.788}$$

where the reduced nuclear mass of  $^{35}\text{Cl}_2$  is given by Eq.(13.787) and the spring constant,  
 10  $k(0)$ , given by Eqs. (11.136) and (13.786) is

$$k(0) = 301.19 \text{ Nm}^{-1} \tag{13.789}$$

The  $^{35}\text{Cl}_2$  transition-state vibrational energy,  $E_{vib}(0)$  or  $\omega_e$ , given by Planck's equation (Eq.  
 (11.127)) is:

$$E_{vib}(0) = \omega_e = \hbar\omega = \hbar 1.01438 \times 10^{14} \text{ rad/s} = 0.06677 \text{ eV} = 538.52 \text{ cm}^{-1} \tag{13.790}$$

15  $\omega_e$ , from the experimental curve fit of the vibrational energies of  $^{35}\text{Cl}_2$  is [28]

$$\omega_e = 559.7 \text{ cm}^{-1} \tag{13.791}$$

Using Eqs. (13.112-13.118) with  $E_{vib}(0)$  given by Eq. (13.790) and  $D_0$  given by Eq.  
 (13.807), the  $^{35}\text{Cl}_2$   $\nu=1 \rightarrow \nu=0$  vibrational energy,  $E_{vib}(1)$  is

$$E_{vib}(1) = 0.0659 \text{ eV} \quad (531.70 \text{ cm}^{-1}) \tag{13.792}$$

20 The experimental vibrational energy of  $^{35}\text{Cl}_2$  using  $\omega_e$  and  $\omega_e x_e$  [28] according to K&P [15]  
 is

$$E_{vib}(1) = 0.0664 \text{ eV} \quad \left( 535.55 \text{ cm}^{-1} \right) \quad (13.793)$$

Using Eq. (13.113) with  $E_{vib}(1)$  given by Eq. (13.792) and  $D_0$  given by Eq. (13.807), the anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{35}\text{Cl}_2$  is

$$\omega_0 x_0 = 3.41 \text{ cm}^{-1} \quad (13.794)$$

5 The experimental anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{35}\text{Cl}_2$  [28] is

$$\omega_0 x_0 = 2.68 \text{ cm}^{-1} \quad (13.795)$$

The vibrational energies of successive states are given by Eqs. (13.790), (13.112), and (13.794).

Using Eqs. (13.133-13.134) and the internuclear distance,  $r = 2c'$ , and reduced mass of  $^{35}\text{Cl}_2$  given by Eqs. (13.768) and (13.787), respectively, the corresponding  $B_e$  is

$$B_e = 0.2420 \text{ cm}^{-1} \quad (13.796)$$

The experimental  $B_e$  rotational parameter of  $^{35}\text{Cl}_2$  is [28]

$$B_e = 0.2440 \text{ cm}^{-1} \quad (13.797)$$

## 15 THE DOPPLER ENERGY TERMS OF $\text{Cl}_2$

The equations of the radiation reaction force of the symmetrical  $\text{Cl}_2$  MO are the given by Eqs. (11.231-11.233) with the substitution of the  $\text{Cl}_2$  parameters and the substitution of the force factor of Eq. (13.761). The angular frequency of the reentrant oscillation in the transition state is

$$20 \quad \omega = \sqrt{\frac{0.93172 \frac{(0.75)}{2} \frac{e^2}{4\pi\epsilon_0 a^3}}{m_e}} = 6.31418 \times 10^{15} \text{ rad/s} \quad (13.798)$$

where  $a$  is given by Eq. (13.766). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 6.31418 \times 10^{15} \text{ rad/s} = 4.15610 \text{ eV} \quad (13.799)$$

In Eq. (11.181), substitution of the total energy of  $\text{Cl}_2$ ,  $E_T(\text{Cl}_2)$ , (Eq. (13.764)) for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.799) for  $\bar{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

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$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(4.15610 \text{ eV})}{m_e c^2}} = -0.12759 \text{ eV} \quad (13.800)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $Cl_2$  due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the 5 electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (13.800) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of  $Cl_2$ . Using the experimental  $^{35}Cl_2$   $\omega_e$  of  $559.7 \text{ cm}^{-1}$  ( $0.06939 \text{ eV}$ ) [28] for  $\bar{E}_{Kvib}$  of the transition state,  $\bar{E}_{osc}(^{35}Cl_2)$  is

$$\bar{E}_{osc}(^{35}Cl_2) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.801)$$

$$10 \quad \bar{E}_{osc}(^{35}Cl_2) = -0.12759 \text{ eV} + \frac{1}{2} (0.06939 \text{ eV}) = -0.09289 \text{ eV} \quad (13.802)$$

### TOTAL AND BOND ENERGIES OF $Cl_2$

$E_{T+osc}(^{35}Cl_2)$ , the total energy of the  $^{35}Cl_2$  radical including the Doppler term, is given by the sum of  $E_T(Cl_2)$  (Eq. (13.764)) and  $\bar{E}_{osc}(^{35}Cl_2)$  given by Eq. (13.802):

$$15 \quad \begin{aligned} E_{T+osc}(^{35}Cl_2) &= V_e + T + V_m + V_p + E_{Coulomb}(Cl, 3sp^3) + \bar{E}_{osc}(^{35}Cl_2) \\ &= E_T(Cl_2) + \bar{E}_{osc}(^{35}Cl_2) \end{aligned} \quad (13.803)$$

$$\begin{aligned} E_{T+osc}(^{35}Cl_2) &= \left\{ \left( \frac{-e^2}{8\pi\epsilon_0 c'} \left[ (0.93172) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.60295 \text{ eV} \right) \right. \\ &\quad \left. \left( 1 + \sqrt{\frac{2\hbar \sqrt{\frac{0.93172(0.75)}{2} \frac{e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \right\} \\ &= -31.63537 \text{ eV} - 0.12759 \text{ eV} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \end{aligned}$$

(13.804)

From Eqs. (13.801-13.804), the total energy of  $^{35}Cl_2$  is



$$\begin{aligned}
 E_{T+osc}({}^{35}\text{Cl}_2) &= -31.63537 \text{ eV} + \bar{E}_{osc}({}^{35}\text{Cl}_2) \\
 &= -31.63537 \text{ eV} - 0.12759 \text{ eV} + \frac{1}{2}(0.06939 \text{ eV}) \\
 &= -31.72826 \text{ eV}
 \end{aligned} \tag{13.805}$$

where the experimental  $\omega_e$  (Eq. (13.791)) was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

The  $\text{Cl}_2$  bond dissociation energy,  $E_D({}^{35}\text{Cl}_2)$ , is given by the difference between the total energies of the two  $\text{Cl}3sp^3$  HOs and  $E_{T+osc}({}^{35}\text{Cl}_2)$ :

$$5 \quad E_D({}^{35}\text{Cl}_2) = 2E_{\text{Coulomb}}(\text{Cl}, 3sp^3) - E_{T+osc}({}^{35}\text{Cl}_2) \tag{13.806}$$

$E_{\text{Coulomb}}(\text{Cl}, 3sp^3)$  is given by Eq. (13.759); thus, the  ${}^{35}\text{Cl}_2$  bond dissociation energy,  $E_D({}^{35}\text{Cl}_2)$ , given by Eqs. (13.759) and (13.805-13.806) is

$$\begin{aligned}
 E_D({}^{35}\text{Cl}_2) &= -2(14.60295 \text{ eV}) - E_{T+osc}({}^{35}\text{Cl}_2) \\
 &= -29.20590 \text{ eV} - (-31.72826 \text{ eV}) \\
 &= 2.52236 \text{ eV}
 \end{aligned} \tag{13.807}$$

The experimental  ${}^{35}\text{Cl}_2$  bond dissociation energy is [49]

$$10 \quad E_D({}^{35}\text{Cl}_2) = 2.51412 \text{ eV} \tag{13.808}$$

The results of the determination of bond parameters of  $\text{Cl}_2$  are given in Table 13.1.

The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

15

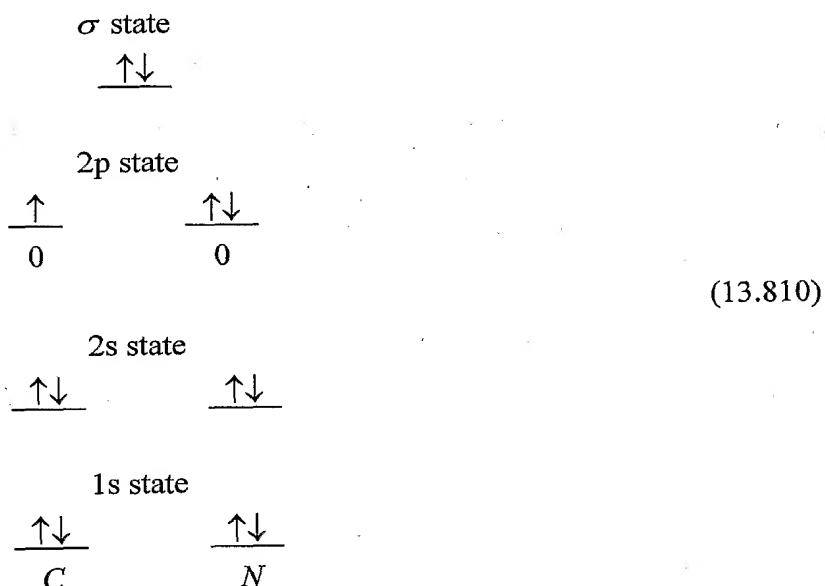
## CARBON NITRIDE RADICAL

The carbon nitride radical can be formed by the reaction of carbon and nitrogen atoms:



The bond in carbon nitride radical comprises a  $H_2$ -type molecular orbital (MO) with two  
20 paired electrons. The force balance equations and radii,  $r_6$  and  $r_7$ , of the  $2p$  shell of  $C$  and  $N$  are derived in the Six-Electron Atoms section and Seven-Electron Atoms section, respectively. With the formation of the  $H_2$ -type MO by the contribution of a  $2p$  electron from each of the  $C$  and  $N$  atoms, a diamagnetic force arises between the remaining  $2p$  electrons of each atom and the  $H_2$ -type MO. This force from each atom causes the  $H_2$ -type

MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining  $2p$  electrons of each atom decrease the radii of the corresponding shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of  $CN$  is  $C1s^2N1s^2C2s^2N2s^2C2p^1N2p^2\sigma_{C,N}^2$  where  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is



10

The carbon nitride radical is predicted to be weakly paramagnetic .

### FORCE BALANCE OF THE $2p$ SHELL OF THE CARBON ATOM OF THE CARBON NITRIDE RADICAL

15 For the  $C$  atom, force balance for the outermost  $2p$  electron of  $CN$  (electron 5) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 5 and the  $2s$ -shell electrons due to spin and orbital angular momentum. The forces used are derived in the Six-Electron Atoms section. The central Coulomb force on the outer-most  $2p$  shell electron of  $CN$  (electron 5) due to the nucleus

20 and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\epsilon_0 r_5^2} \mathbf{i}_r
 \tag{13.811}$$

for  $r > r_4$ . The  $2p$  shell possess an external electric field given by Eq. (10.92) for  $r > r_5$ .

The single unpaired carbon  $2p$  electron gives rise to a diamagnetic force on the  $\sigma$ -MO as given by Eqs. (13.835-13.839). The corresponding Newtonian reaction force cancels  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82). The energy is minimized with conservation of angular momentum.

5 This condition is met when

$$\mathbf{F}_{diamagnetic} = 0 \quad (13.812)$$

And,  $\mathbf{F}_{mag\ 2}$  corresponding to the maximum orbital angular momentum of the three  $2p$  orbitals given by Eq. (10.89) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{3\hbar^2}{m_e r_5^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (13.813)$$

10 The electric field external to the  $2p$  shell given by Eq. (10.92) for  $r > r_5$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is :

$$\mathbf{F}_{diamagnetic\ 2} = - \left[ \frac{Z-5}{Z-4} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{m_e r_5^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (13.814)$$

The radius of the  $2p$  shell is calculated by equating the outward centrifugal force to  
15 the sum of the electric (Eq. (13.811)) and diamagnetic (Eqs. (13.812) and (13.814)), and paramagnetic (Eq. (13.813)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \left( \frac{(Z-4)e^2}{4\pi\epsilon_0 r_5^2} + \frac{3\hbar^2}{Z m_e r_5^2 r_3} \sqrt{s(s+1)} - \left[ \frac{Z-5}{Z-4} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_5^4 m_e} 10 \sqrt{s(s+1)} \right) \quad (13.815)$$

Substitution of  $v_5 = \frac{\hbar}{m_e r_5}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.815) gives:

$$\frac{\hbar^2}{m_e r_5^3} = \frac{(Z-4)e^2}{4\pi\epsilon_0 r_5^2} + \frac{3\hbar^2}{Z m_e r_5^2 r_3} \sqrt{\frac{3}{4}} - \left[ \frac{Z-5}{Z-4} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_5^4 m_e} 10 \sqrt{\frac{3}{4}} \quad (13.816)$$

20 The quadratic equation corresponding to Eq. (13.816) is

$$r_5^2 - \frac{\frac{\hbar^2}{m_e}}{\left( \frac{(Z-4)e^2}{4\pi\epsilon_0} + \frac{3\hbar^2}{Z m_e r_3} \sqrt{\frac{3}{4}} \right)} r_5 - \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-5}{Z-4} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-4)e^2}{4\pi\epsilon_0} + \frac{3\hbar^2}{Z m_e r_3} \sqrt{\frac{3}{4}} \right)} = 0$$

(13.817)

The solution of Eq. (13.817) using the quadratic formula is:

$$r_s = \frac{a_0}{\left( (Z-4) + \frac{3\sqrt{3}}{Z2r_3} \right)} \pm a_0 \sqrt{\frac{1}{\left( (Z-4) + \frac{3\sqrt{3}}{Z2r_3} \right)^2} + \frac{20\sqrt{3} \left( \left[ \frac{Z-5}{Z-4} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 \right)}{\left( (Z-4) + \frac{3\sqrt{3}}{Z2r_3} \right)}} \quad (13.818)$$

$r_3$  in units of  $a_0$

The positive root of Eq. (13.818) must be taken in order that  $r_s > 0$ . Substitution of

5  $\frac{r_3}{a_0} = 0.84317$  (Eq. (10.62) with  $Z = 6$ ) into Eq. (13.818) gives

$$r_s = 0.88084a_0 \quad (13.819)$$

## FORCE BALANCE OF THE $2p$ SHELL OF THE NITROGEN ATOM OF THE CARBON NITRIDE RADICAL

- 10 For the  $N$  atom, force balance for the outermost  $2p$  electron of  $CN$  (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other  $2p$ -shell as well as the  $2s$ -shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central Coulomb force on the outer-most  $2p$  shell electron of  $CN$
- 15 (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} \mathbf{i}_r \quad (13.820)$$

for  $r > r_s$ . The  $2p$  shell possess an external electric field given by Eq. (10.92) for  $r > r_6$ .

The forces to determine the radius of the  $N2p$  shell of  $N$  in  $CN$  are the same as

20 those of  $N$  in  $N_2$  except that in  $CN$  there is a contribution from the Newtonian reaction force that arises from the single unpaired carbon  $2p$  electron. The energy is minimized with

conservation of angular momentum. This condition is met when  $\mathbf{F}_{\text{diamagnetic}}$  of  $N$  in  $CN$  is canceled by the  $\sigma$ -MO-reaction force. Eq. (13.622) becomes

$$\mathbf{F}_{\text{diamagnetic}} = 0 \quad (13.821)$$

And,  $\mathbf{F}_{\text{mag } 2}$  corresponding to the conserved orbital angular momentum of the three orbitals  
5 given by Eq. (10.89) is

$$\mathbf{F}_{\text{mag } 2} = \frac{1}{Z} \frac{3\hbar^2}{m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (13.822)$$

The electric field external to the  $2p$  shell given by Eq. (10.92) for  $r > r_6$  gives rise to a second diamagnetic force,  $\mathbf{F}_{\text{diamagnetic } 2}$ , given by Eq. (10.93).  $\mathbf{F}_{\text{diamagnetic } 2}$  due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is

$$10 \quad \mathbf{F}_{\text{diamagnetic } 2} = -\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (13.823)$$

The  $N$  forces  $\mathbf{F}_{\text{ele}}$ ,  $\mathbf{F}_{\text{mag } 2}$ ,  $\mathbf{F}_{\text{diamagnetic } 2}$ , and  $\mathbf{F}_{\text{mag } 3}$  of  $CN$  are the same as those of  $N_2$  given by Eqs. (13.621) and (13.623-13.624), respectively. In both cases, the contribution of a  $2p$  electron from the  $N$  atom in the formation of the  $\sigma$  MO gives rise to a paramagnetic force on the remaining two  $2p$  electrons that pair. Thus, the force,  $\mathbf{F}_{\text{mag } 3}$  of  $CN$ , given by  
15 Eq. (13.625) is

$$\mathbf{F}_{\text{mag } 3} = \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \mathbf{i}_r \quad (13.824)$$

The radius of the  $2p$  shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.820)) and diamagnetic (Eqs. (13.821) and (13.823)), and paramagnetic (Eqs. (13.822) and (13.824)) forces as follows:

$$20 \quad \frac{m_e v_6^2}{r_6} = \left( \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} + \frac{3\hbar^2}{Zm_e r_6^2 r_3} \sqrt{s(s+1)} - \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \right) \quad (13.825)$$

Substitution of  $v_6 = \frac{\hbar}{m_e r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.626) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3} \sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} + \frac{3\hbar^2}{Zm_e r_6^2 r_3} \sqrt{\frac{3}{4}} - \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{\frac{3}{4}} \quad (13.826)$$

The quadratic equation corresponding to Eq. (13.826) is

$$r_6^2 - \frac{\frac{\hbar^2}{m_e} \left(1 - \frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-5)e^2}{4\pi\epsilon_0} + \frac{3\hbar^2}{Zm_e r_3} \sqrt{\frac{3}{4}}\right)} r_6 - \frac{\frac{\hbar^2}{m_e} \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) r_3 10 \sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\epsilon_0} + \frac{3\hbar^2}{Zm_e r_3} \sqrt{\frac{3}{4}}\right)} = 0 \quad (13.827)$$

The solution of Eq. (13.827) using the quadratic formula is:

$$r_6 = \frac{a_0 \left(1 - \frac{\sqrt{3}}{8}\right)}{\left((Z-5) + \frac{3\sqrt{3}}{Z2r_3}\right)} \pm a_0 \sqrt{\frac{\left(\frac{1 - \frac{\sqrt{3}}{8}}{\left((Z-5) + \frac{3\sqrt{3}}{Z2r_3}\right)}\right)^2}{2} + \frac{20\sqrt{3} \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) r_3}{\left((Z-5) + \frac{3\sqrt{3}}{Z2r_3}\right)}} \quad (13.828)$$

$r_3$  in units of  $a_0$

The positive root of Eq. (13.828) must be taken in order that  $r_6 > 0$ . Substitution of

$\frac{r_3}{a_0} = 0.69385$  (Eq. (10.62) with  $Z = 7$ ) into Eq. (13.828) gives

$$r_6 = 0.76366a_0 \quad (13.829)$$

## 10 ENERGIES OF THE $2p$ SHELLS OF THE CARBON AND NITROGEN ATOMS OF THE CARBON NITRIDE RADICAL

The central forces on the  $2p$  shell of the  $C$  and  $N$  atoms are increased with the formation of the  $\sigma$  MO which reduces each shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the  $C$  and  $N$  atoms at the new radii are calculated and added to the energy of the  $\sigma$  MO to give the total energy of  $CN$ . Then, the bond energy is determined from the total  $CN$  energy.

The radius  $r_6$  of the carbon atom before bonding is given by Eq. (10.122):

$$r_6 = 1.20654a_0 \quad (13.830)$$

Using the initial radius  $r_6$  of the  $C$  atom and the final radius  $r_3$  of the  $C2p$  shell of  $CN$  (Eq.

(13.819)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(CN, C2p)$  of the Coulombic energy change of the  $C2p$  electron is determined using Eq. (10.102):

$$E_T(CN, C2p) = -\sum_{n=4}^4 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_5} - \frac{1}{r_6} \right) = -(13.60580 \text{ eV})(0.30647)(2) = -8.33948 \text{ eV}$$

5 (13.831)

The radius  $r_7$  of the nitrogen atom before bonding is given by Eq. (10.142):

$$r_7 = 0.93084a_0 \quad (13.832)$$

Using the initial radius  $r_7$  of the  $N$  atom and the final radius  $r_6$  of the  $N2p$  shell of  $CN$  (Eq. (13.829)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(CN, N2p)$  of the Coulombic energy change of the  $N2p$  electron is determined using Eq. (10.102):

10

$$\begin{aligned} E_T(CN, N2p) &= -\sum_{n=4}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_7} \right) \\ &= -(13.60580 \text{ eV})(0.23518)(2+3) \\ &= -15.99929 \text{ eV} \end{aligned} \quad (13.833)$$

### FORCE BALANCE OF THE $\sigma$ MO OF THE CARBON NITRIDE RADICAL

15 The diamagnetic force  $\mathbf{F}_{\text{diamagneticMO1}}$  for the  $\sigma$ -MO of the  $CN$  molecule due to the two paired electrons in the  $N2p$  shell given by Eq. (13.633) with  $n_e = 2$  is:

$$\mathbf{F}_{\text{diamagneticMO1}} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \quad (13.834)$$

The force  $\mathbf{F}_{\text{diamagneticMO2}}$  is given by Eq. (13.634) except that the force is the summed over the individual diamagnetic-force terms due to each component of angular momentum  $|L_i|$  acting on the electrons of the  $\sigma$ -MO from each atom having a nucleus of charge  $Z_j$  at one of the foci of the  $\sigma$ -MO:

20

$$\mathbf{F}_{\text{diamagneticMO2}} = \sum_{i,j} \frac{|L_i| \hbar}{Z_j 2m_e a^2 b^2} D\mathbf{i}_\xi \quad (13.835)$$

Using Eqs. (11.200), (13.633-13.634), and (13.834-13.835), the force balance for the  $\sigma$ -MO of the carbon nitride radical comprising carbon with charge  $Z_1 = 6$  and  $|L_1| = \hbar$  and

$|L_2| = \sqrt{\frac{3}{4}}\hbar$  and nitrogen with  $Z_2 = 7$  and  $|L_3| = \hbar$  is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left( 1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.836)$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 ab^2} D - \left( \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.837)$$

$$\left( 2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 ab^2} D \quad (13.838)$$

$$5 \quad a = \left( 2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) a_0 \quad (13.839)$$

Substitution of  $Z_1 = 6$  and  $Z_2 = 7$  into Eq. (13.839) gives

$$a = 2.45386a_0 = 1.29853 \times 10^{-10} \text{ m} \quad (13.840)$$

Substitution of Eq. (13.840) into Eq. (11.79) is

$$c' = 1.10767a_0 = 5.86153 \times 10^{-11} \text{ m} \quad (13.841)$$

10 The internuclear distance given by multiplying Eq. (13.841) by two is

$$2c' = 2.21534a_0 = 1.17231 \times 10^{-10} \text{ m} \quad (13.842)$$

The experimental bond distance from Ref. [28] is

$$2c' = 1.17181 \times 10^{-10} \text{ m} \quad (13.843)$$

Substitution of Eqs. (13.840-13.841) into Eq. (11.80) is

$$15 \quad b = c = 2.18964a_0 = 1.15871 \times 10^{-10} \text{ m} \quad (13.844)$$

Substitution of Eqs. (13.840-13.841) into Eq. (11.67) is

$$e = 0.45140 \quad (13.845)$$

Using the electron configuration of CN (Eq. (13.810), the radii of the  $Cl s = 0.17113a_0$  (Eq.

(10.51)),  $C2s = 0.84317a_0$  (Eq. (10.62)),  $C2p = 0.88084a_0$  (Eq. (13.819)),  $N1s = 0.14605a_0$

20 (Eq. (10.51)),  $N2s = 0.69385a_0$  (Eq. (10.62)), and  $N2p = 0.76366a_0$  (Eq. (13.829)) shells



and the parameters of the  $\sigma$  MO of CN given by Eqs. (13.3-13.4), (13.840-13.842), and (13.844-13.845), the dimensional diagram and charge-density of the CN MO are shown in Figures 27 and 28, respectively.

## 5 SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE CARBON NITRIDE RADICAL

The energies of the CN  $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. (13.840-13.841) and (13.844)) into the energy equations (Eqs. (11.207-11.212)) of  $H_2$ :

$$V_e = \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -23.90105 \text{ eV} \quad (13.846)$$

$$10 \quad V_p = \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 12.28328 \text{ eV} \quad (13.847)$$

$$T = \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 4.87009 \text{ eV} \quad (13.848)$$

$$V_m = \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -2.43504 \text{ eV} \quad (13.849)$$

$$E_T = V_e + T + V_m + V_p \quad (13.850)$$

Substitution of Eqs. (11.79) and (13.846-13.849) into Eq. (13.850) gives

$$15 \quad E_T(CN, \sigma) = \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left( \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right) = -9.18273 \text{ eV} \quad (13.851)$$

where  $E_T(CN, \sigma)$  is the total energy of the  $\sigma$  MO of CN. The sum,  $E_T(CN)$ , of  $E_T(CN, C2p)$ , the C2p AO contribution given by Eq. (13.831),  $E_T(CN, N2p)$ , the N2p AO contribution given by Eq. (13.833), and  $E_T(CN, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (13.851) is:

$$\begin{aligned} E_T(CN) &= E_T(CN, C2p) + E_T(CN, N2p) + E_T(CN, \sigma) \\ 20 \quad &= -8.33948 \text{ eV} - 15.99929 \text{ eV} - 9.18273 \text{ eV} \\ &= -33.52149 \text{ eV} \end{aligned} \quad (13.852)$$

VIBRATION OF  $CN$ 

The vibrational energy levels of  $CN$  may be solved by determining the Morse potential curve from the energy relationships for the transition from a  $C$  atom and  $N$  atom whose parameters are given by Eqs. (10.115-10.123) and (10.134-10.143), respectively, to a  $C$  atom  
 5 whose parameter  $r_5$  is given by Eq. (10.819), a  $N$  atom whose parameter  $r_6$  is given by Eq. (13.829), and the  $\sigma$  MO whose parameters are given by Eqs. (13.840-13.842) and (13.844-13.845). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter  
 10 (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF THE CARBON NITRIDE RADICAL

15 The equations of the radiation reaction force of  $CN$  are the same as those of  $H_2$  with the substitution of the  $CN$  parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{e^2}{4\pi\epsilon_0 a^3}} = 1.07550 \times 10^{16} \text{ rad/s} \quad (13.853)$$

where  $a$  is given by Eq. (13.840). The kinetic energy,  $E_K$ , is given by Planck's equation  
 20 (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 1.07550 \times 10^{16} \text{ rad/s} = 7.07912 \text{ eV} \quad (13.854)$$

In Eq. (11.181), substitution of  $E_T(CN)$  for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.854) for  $\bar{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -33.59603 \text{ eV} \sqrt{\frac{2e(7.07912 \text{ eV})}{m_e c^2}} = -0.17684 \text{ eV} \quad (13.855)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the  $CN$  MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation

of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (13.855) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental CN  $\omega_e$  of  $2068.59 \text{ cm}^{-1}$  ( $0.25647 \text{ eV}$ ) [28] for  $\bar{E}_{Kvib}$  of the transition state,  $\bar{E}_{osc}(CN)$  is

$$5 \quad \bar{E}_{osc}(CN) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.856)$$

$$\bar{E}_{osc}(CN) = -0.17684 \text{ eV} + \frac{1}{2} (0.25647 \text{ eV}) = -0.04860 \text{ eV} \quad (13.857)$$

### TOTAL AND BOND ENERGIES OF THE CARBON NITRIDE RADICAL

$E_{T+osc}(CN)$ , the total energy of CN including the Doppler term, is given by the sum of  
10  $E_T(CN)$  (Eq. (13.852)) and  $\bar{E}_{osc}(CN)$  given by Eq. (13.857):

$$\begin{aligned} E_{T+osc}(CN) &= V_e + T + V_m + V_p + E_T(CN, C2p) + E_T(CN, N2p) + \bar{E}_{osc}(CN) \\ &= E_T(CN, \sigma) + E_T(CN, C2p) + E_T(CN, N2p) + \bar{E}_{osc}(CN) \\ &= E_T(CN) + \bar{E}_{osc}(CN) \end{aligned} \quad (13.858)$$

$$\begin{aligned} E_{T+osc}(CN) &= \left\{ \left( \frac{-e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2}}} \left( \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right) \right. \right. \\ &\quad \left. \left. - \sum_{C,n=4}^4 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_5} - \frac{1}{r_6} \right) - \sum_{N,n=4}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_7} \right) \right) \right. \\ &\quad \left. \left( 1 + \sqrt{\frac{2\hbar \sqrt{\frac{e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} \right) + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right\} \\ &= -33.52149 \text{ eV} - 0.17684 \text{ eV} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \end{aligned} \quad (13.859)$$

From Eqs. (13.856-13.859), the total energy of the CN MO is

$$\begin{aligned} E_{T+osc}(CN) &= -33.52149 \text{ eV} + \bar{E}_{osc}(CN) \\ &= -33.52149 \text{ eV} - 0.17684 \text{ eV} + \frac{1}{2} (0.25647 \text{ eV}) \\ &= -33.56970 \text{ eV} \end{aligned} \quad (13.860)$$

where the experimental  $\omega_e$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

The  $CN$  bond dissociation energy,  $E_D(CN)$ , is given by the difference between the sum of the energies of the  $C$  and  $N$  atoms and  $E_{T+osc}(CN)$ :

$$E_D(CN) = E(C) + E(N) - E_{T+osc}(CN) \quad (13.861)$$

5 where the energy of a carbon atom is [6]

$$E(C) = -11.26030 \text{ eV} \quad (13.862)$$

and the energy of a nitrogen atom is [6]

$$E(N) = -14.53414 \text{ eV} \quad (13.863)$$

Thus, the  $CN$  bond dissociation energy,  $E_D(CN)$ , given by Eqs. (13.860-13.863) is

$$\begin{aligned} E_D(CN) &= -(11.26030 \text{ eV} + 14.53414 \text{ eV}) - E_{T+osc}(CN) \\ 10 \quad &= -25.79444 \text{ eV} - (-33.56970 \text{ eV}) \\ &= 7.77526 \text{ eV} \end{aligned} \quad (13.864)$$

The experimental  $CN$  bond dissociation energy is [50]

$$E_{D298}(CN) = 7.7731 \text{ eV} \quad (13.865)$$

The results of the determination of bond parameters of  $CN$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations  
15 containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

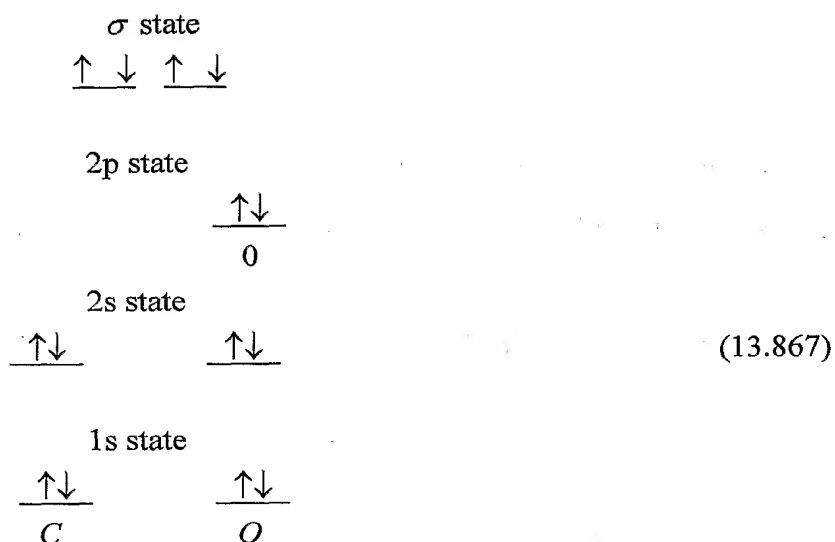
## CARBON MONOXIDE MOLECULE

The carbon monoxide molecule can be formed by the reaction of carbon and oxygen atoms:



The bond in the carbon monoxide molecule comprises a double bond, a  $H_2$ -type molecular orbital (MO) with four paired electrons. The force balance equation and radius  $r_6$  of the  $2p$  shell of  $C$  is derived in the Six-Electron Atoms section. The force balance equation and radius  $r_8$  of the  $2p$  shell of  $O$  is derived in the Eight-Electron Atoms section. With the  
25 formation of the  $H_2$ -type MO by the contribution of two  $2p$  electrons from each of the  $C$  and  $O$  atoms, a diamagnetic force arises between the remaining outer shell atomic electrons, the  $2s$  electrons of  $C$  and the  $2p$  electrons of  $O$ , and the  $H_2$ -type MO. This force from  $C$

and  $O$  causes the  $H_2$ -type MO to move to greater principal axes than would result with the Coulombic force alone. But, the factor of two increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining  $O2p$  electrons decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of  $CO$  is  $C1s^2O1s^2C2s^2O2s^2O2p^2\sigma_{C,O}^4$  where  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is



Carbon monoxide is predicted to be diamagnetic in agreement with observations [42].

10

# FORCE BALANCE OF THE $2p$ SHELL OF THE OXYGEN ATOM OF THE CARBON MONOXIDE MOLECULE

For the  $O$  atom, force balance for the outermost  $2p$  electron of  $CO$  (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other  $2p$  electron as well as the  $2s$ -shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most  $2p$  shell electron of  $CO$  (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} \mathbf{i}_r \tag{13.868}$$

20

for  $r > r_5$ . The  $2p$  shell possess a +2 external electric field given by Eq. (10.92) for  $r > r_6$ . The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force,  $\mathbf{F}_{\text{diamagnetic}}$ , of Eq. (10.82) due to the  $p$ -orbital contribution is given by:

$$5 \quad \mathbf{F}_{\text{diamagnetic}} = -\left(\frac{1}{3}\right) \frac{\hbar^2}{4m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r \quad (13.869)$$

And,  $\mathbf{F}_{\text{mag } 2}$  corresponding to the conserved spin and orbital angular momentum given by Eq. (10.157) is

$$\mathbf{F}_{\text{mag } 2} = \frac{1}{Z} \frac{2\hbar^2}{m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (13.870)$$

The electric field external to the  $2p$  shell given by Eq. (10.92) for  $r > r_6$  gives rise to a second diamagnetic force,  $\mathbf{F}_{\text{diamagnetic } 2}$ , given by Eq. (10.93).  $\mathbf{F}_{\text{diamagnetic } 2}$  due to the binding of the  $p$ -orbital electron having an electric field of +2 outside of its radius is :

$$\mathbf{F}_{\text{diamagnetic } 2} = -\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (13.871)$$

In addition, the contribution of two  $2p$  electrons in the formation of the  $\sigma$  molecular orbital (MO) gives rise to a paramagnetic force on the remaining paired  $2p$  electrons. The force  $\mathbf{F}_{\text{mag } 3}$  is given by Eq. (13.625) wherein the radius is  $r_6$  :

$$\mathbf{F}_{\text{mag } 3} = \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \mathbf{i}_r \quad (13.872)$$

The radius of the  $2p$  shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.868)) and diamagnetic (Eqs. (13.869) and (13.871)), and paramagnetic (Eqs. (13.870) and (13.872)) forces as follows:

$$20 \quad \frac{m_e v_6^2}{r_6} = \left( \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{\hbar^2}{12m_e r_6^2 r_3} \sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{s(s+1)} - \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \right) \quad (13.873)$$

Substitution of  $v_6 = \frac{\hbar}{m_e r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.873) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3} \sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{\frac{3}{4}} - \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{\frac{3}{4}}$$

(13.874)

The quadratic equation corresponding to Eq. (13.874) is

$$r_6^2 - \frac{\frac{\hbar^2}{m_e} \left(1 - \frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-5)e^2}{4\pi\epsilon_0} - \left(\frac{1}{12} - \frac{2}{Z}\right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)} r_6 - \frac{\frac{\hbar^2}{m_e} \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) r_3 10 \sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\epsilon_0} - \left(\frac{1}{12} - \frac{2}{Z}\right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)} = 0 \quad (13.875)$$

The solution of Eq. (13.875) using the quadratic formula is:

$$r_6 = \frac{a_0 \left(1 - \frac{\sqrt{3}}{8}\right)}{\left((Z-5) - \left(\frac{1}{12} - \frac{2}{Z}\right) \frac{\sqrt{3}}{2r_3}\right)} \pm a_0 \frac{\left[\left(\frac{1 - \frac{\sqrt{3}}{8}}{\left((Z-5) - \left(\frac{1}{12} - \frac{2}{Z}\right) \frac{\sqrt{3}}{2r_3}\right)}\right)^2 - 20\sqrt{3} \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) r_3\right]}{\left((Z-5) - \left(\frac{1}{12} - \frac{2}{Z}\right) \frac{\sqrt{3}}{2r_3}\right)} \quad (13.876)$$

$r_3$  in units of  $a_0$

The positive root of Eq. (13.876) must be taken in order that  $r_6 > 0$ . Substitution of

$\frac{r_3}{a_0} = 0.59020$  (Eq. (10.62) with  $Z = 8$ ) into Eq. (13.876) gives

$$r_6 = 0.68835 a_0 \quad (13.877)$$

## 10 ENERGIES OF THE $2s$ AND $2p$ SHELLS OF THE CARBON ATOM AND THE $2p$ SHELL OF THE OXYGEN ATOM OF THE CARBON MONOXIDE MOLECULE

With the formation of the  $H_2$ -type MO by the contribution of two  $2p$  electrons from the C atom, the remaining outer-shell atomic electrons comprise the  $2s$  electrons, which are unchanged by bonding with oxygen. However, the total energy of the CO molecule, which is subtracted from the sum of the energies of the carbon and oxygen atoms to determine the bond energy, is increased by the ionization energies of  $C^+$  and  $O^+$  given by Eqs. (10.113-10.114) and (10.152-10.153), respectively. Experimentally, the energies are [6]

$$E(\text{ionization}; C^+) = 24.38332 \text{ eV} \quad (13.878)$$

$$E(\text{ionization}; O^+) = 35.11730 \text{ eV} \quad (13.879)$$

In addition, the central forces on the  $2p$  shell of the  $O$  atom are increased with the formation of the  $\sigma$  MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the  $O$  atom at the new radius are calculated and added to the ionization energies of  $C^+$  and  $O^+$ , and the energy of the  $\sigma$  MO to give the total energy of  $CO$ . Then, the bond energy is determined from the total  $CO$  energy.

The radius  $r_8$  of the oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 \quad (13.880)$$

Using the initial radius  $r_8$  of the  $O$  atom and the final radius  $r_6$  of the  $O2p$  shell (Eq. (13.877)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(O, 2p)$  of the Coulombic energy change of the  $O2p$  electrons of the  $O$  atom is determined using Eq. (10.102):

$$\begin{aligned} E_T(O, 2p) &= -\sum_{n=4}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_8} \right) \\ &= -(13.60580 \text{ eV})(0.45275)(3+4) \\ &= -43.11996 \text{ eV} \end{aligned} \quad (13.881)$$

## 15 FORCE BALANCE OF THE $\sigma$ MO OF THE CARBON MONOXIDE MOLECULE

The force balance can be considered due to a second pair of two electrons binding to a molecular ion having  $+2e$  at each focus and a first bound pair. Then, the forces are the same as those of a molecule ion having  $+e$  at each focus. The diamagnetic force  $\mathbf{F}_{\text{diamagneticMO1}}$  for the  $\sigma$ -MO of the  $CO$  molecule due to the two paired electrons in each of the  $C2s$  and  $O2p$  shells is given by Eq. (13.633) with  $n_e = 2$ :

$$\mathbf{F}_{\text{diamagneticMO1}} = \frac{\hbar^2}{2m_e a^2 b^2} D \mathbf{i}_\xi \quad (13.882)$$

The force  $\mathbf{F}_{\text{diamagneticMO2}}$  is given by Eqs. (13.634) and (13.835) as the sum of the contributions due to carbon with  $Z = Z_1$  and oxygen with  $Z = Z_2$ .  $\mathbf{F}_{\text{diamagneticMO1}}$  for  $CO$  with  $|L_i| = \hbar$  is

$$\mathbf{F}_{\text{diamagneticMO2}} = \left( \frac{1}{Z_1} + \frac{1}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D \mathbf{i}_\xi \quad (13.883)$$



The force balance equation for the  $\sigma$ -MO of the carbon monoxide molecule given by Eqs. (11.200), (13.633-13.634), and (13.882-13.883) is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \left(\frac{1}{Z_1} + \frac{1}{Z_2}\right)\right) \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.884)$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D - \left(\frac{1}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.885)$$

$$5 \quad \left(2 + \frac{1}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D \quad (13.886)$$

$$a = \left(2 + \frac{1}{Z_1} + \frac{1}{Z_2}\right) a_0 \quad (13.887)$$

Substitution of  $Z_1 = 6$  and  $Z_2 = 8$  into Eq. (13.887) gives

$$a = 2.29167a_0 = 1.21270 \times 10^{-10} \text{ m} \quad (13.888)$$

Substitution of Eq. (13.888) into Eq. (11.79) is

$$10 \quad c' = 1.07044a_0 = 5.66450 \times 10^{-11} \text{ m} \quad (13.889)$$

The internuclear distance given by multiplying Eq. (13.889) by two is

$$2c' = 2.14087a_0 = 1.13290 \times 10^{-10} \text{ m} \quad (13.890)$$

The experimental bond distance is [28]

$$2c' = 1.12823 \times 10^{-10} \text{ m} \quad (13.891)$$

15 Substitution of Eqs. (13.888-13.889) into Eq. (11.80) is

$$b = c = 2.02630a_0 = 1.07227 \times 10^{-10} \text{ m} \quad (13.892)$$

Substitution of Eqs. (13.888-13.889) into Eq. (11.67) is

$$e = 0.46710 \quad (13.893)$$

Using the electron configuration of  $CO$  (Eq. (13.867)), the radii of the  $C1s = 0.17113a_0$  (Eq. (10.51)),  $C2s = 0.84317a_0$  (Eq. (10.62)),  $O1s = 0.12739a_0$  (Eq. (10.51)),  $O2s = 0.59020a_0$  (Eq. (10.62)), and  $O2p = 0.68835a_0$  (Eq. (13.877)) shells and the parameters of the  $\sigma$  MO of  $CO$  given by Eqs. (13.3-13.4), (13.888-13.890), and (13.892-13.893), the dimensional diagram and charge-density of the  $CO$  MO are shown in Figures 29 and 30, respectively.

# SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE CARBON MONOXIDE MOLECULE

The energies of the  $CO$   $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. 5 (13.888-13.889) and (13.892)) into the energy equations (Eqs. (11.207-11.212)) of  $H_2$  except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the  $\sigma$ -MO double bond with two pairs of paired electrons:

$$V_e = 2^2 \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -102.97635 \text{ eV} \quad (13.894)$$

$$V_p = 2^2 \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 50.84210 \text{ eV} \quad (13.895)$$

$$10 \quad T = 2 \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 11.23379 \text{ eV} \quad (13.896)$$

$$V_m = 2^2 \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -11.23379 \text{ eV} \quad (13.897)$$

$$E_T = V_e + T + V_m + V_p \quad (13.898)$$

Substitution of Eqs. (11.79) and (13.894-13.897) into Eq. (13.898) gives

$$E_T(CO, \sigma) = \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left( 8 \ln \frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}} - 4 \right) = -52.13425 \text{ eV} \quad (13.899)$$

15 where  $E_T(CO, \sigma)$  is the total energy of the  $\sigma$  MO of  $CO$ . The total energy of  $CO$ ,  $E_T(CO)$ , is given by the sum of  $E(\text{ionization}; C^+)$ , the energy of the second electron of carbon (Eq. (13.878)) donated to the double bond,  $E(\text{ionization}; O^+)$ , the energy of the second electron of oxygen (Eq. (13.879)) donated to the double bond,  $E_T(O, 2p)$ , the  $O2p$  AO contribution due to the decrease in radius with bond formation (Eq. (13.881)), and  
20  $E_T(CO, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (13.899):

$$\begin{aligned} E_T(CO) &= E(\text{ionization}; C^+) + E(\text{ionization}; O^+) + E_T(O, 2p) + E_T(CO, \sigma) \\ &= 24.38332 \text{ eV} + 35.11730 \text{ eV} - 43.11996 \text{ eV} - 52.13425 \text{ eV} \\ &= -35.75359 \text{ eV} \end{aligned} \quad (13.900)$$

## VIBRATION OF CO

The vibrational energy levels of CO may be solved by determining the Morse potential curve from the energy relationships for the transition from a C atom and O atom whose parameters are given by Eqs. (10.115-10.123) and (10.154-10.163), respectively, to a C atom whose parameter  $r_4$  is given by Eq. (10.61), an O atom whose parameter  $r_6$  is given by Eq. (13.877), and the  $\sigma$  MO whose parameters are given by Eqs. (13.888-13.890) and (13.892-13.893). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF THE CARBON MONOXIDE MOLECULE

The equations of the radiation reaction force of carbon monoxide are the same as those of  $H_2$  with the substitution of the CO parameters except that there is a factor of four increase in the central force in Eq. (11.231) due to the double bond. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{4e^2}{4\pi\epsilon_0 a^3}}{m_e}} = 2.38335 \times 10^{16} \text{ rad/s} \quad (13.901)$$

where  $a$  is given by Eq. (13.888). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.38335 \times 10^{16} \text{ rad/s} = 15.68762 \text{ eV} \quad (13.902)$$

In Eq. (11.181), substitution of  $E_T(CO)$  for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.902) for  $\bar{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -35.75359 \text{ eV} \sqrt{\frac{2e(15.68762 \text{ eV})}{m_e c^2}} = -0.28016 \text{ eV} \quad (13.903)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the  $CO$  MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given  
 5 by Eq. (13.903) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental  $CO$   $\omega_e$  of  $2169.81\text{ cm}^{-1}$  ( $0.26902\text{ eV}$ ) [28] for  $\bar{E}_{Kvib}$  of the transition state,  $\bar{E}'_{osc}(CO)$  per bond is

$$\bar{E}'_{osc}(CO) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.904)$$

$$\bar{E}'_{osc}(CO) = -0.28016\text{ eV} + \frac{1}{2}(0.26902\text{ eV}) = -0.14564\text{ eV} \quad (13.905)$$

10 Since the  $\sigma$  MO bond is a double bond with twice as many electrons as a single bond,  $\bar{E}'_{osc}(CO)$  is multiplied by two to give

$$\bar{E}_{osc}(CO) = -0.29129\text{ eV} \quad (13.906)$$

## 15 TOTAL AND BOND ENERGIES OF THE CARBON MONOXIDE MOLECULE

$E_{T+osc}(CO)$ , the total energy of  $CO$  including the Doppler term, is given by the sum of  $E_T(CO)$  (Eq. (13.900)) and  $\bar{E}_{osc}(CO)$  given by Eq. (13.906):

$$\begin{aligned} E_{T+osc}(CO) &= \left( V_e + T + V_m + V_p + E(\text{ionization}; C^+) \right. \\ &\quad \left. + E(\text{ionization}; O^+) + E_T(O, 2p) + \bar{E}_{osc}(CO) \right) \\ &= \left( E_T(CO, \sigma) + E(\text{ionization}; C^+) + E(\text{ionization}; O^+) \right. \\ &\quad \left. + E_T(O, 2p) + \bar{E}_{osc}(CO) \right) \\ &= E_T(CO) + \bar{E}_{osc}(CO) \end{aligned} \quad (13.907)$$

$$\begin{aligned}
E_{T+osc}(CO) &= \left\{ \left[ \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left( \frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}} - 4 \right) + E(\text{ionization}; C^+) \right] \right. \\
&\quad \left. + E(\text{ionization}; O^+) - \sum_{O,n=4}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_8} \right) \right. \\
&\quad \left. \left[ \frac{1+2\sqrt{\frac{2\hbar\sqrt{\frac{4e^2}{4\pi\epsilon_0 a^3}}}{m_e}}}{m_e c^2} \right] + 2 \left( \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \right\} \quad (13.908) \\
&= -35.75359 \text{ eV} - 2(0.28016 \text{ eV}) + 2 \left( \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)
\end{aligned}$$

From Eqs. (13.906-13.908), the total energy of the CO MO is

$$\begin{aligned}
E_{T+osc}(CO) &= -35.75359 \text{ eV} + \bar{E}_{osc}(CO) \\
&= -35.75359 \text{ eV} + (-0.29129 \text{ eV}) \\
&= -36.04488 \text{ eV} \quad (13.909)
\end{aligned}$$

where the experimental  $\omega_e$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

- 5 The CO bond dissociation energy,  $E_D(CO)$ , is given by the difference between the sum of the energies of the C and O atoms and  $E_{T+osc}(CO)$ :

$$E_D(CO) = E(C) + E(O) - E_{T+osc}(CO) \quad (13.910)$$

where the energy of a carbon atom is [6]

$$E(C) = -11.26030 \text{ eV} \quad (13.911)$$

- 10 and the energy of an oxygen atom is [6]

$$E(O) = -13.61806 \text{ eV} \quad (13.912)$$

Thus, the CO bond dissociation energy,  $E_D(CO)$ , given by Eqs. (13.909-13.912) is

$$\begin{aligned}
E_D(CO) &= -(11.26030 \text{ eV} + 13.61806 \text{ eV}) - E_{T+osc}(CO) \\
&= -24.87836 \text{ eV} - (-36.04488 \text{ eV}) \\
&= 11.16652 \text{ eV} \quad (13.913)
\end{aligned}$$

The experimental CO bond dissociation energy is [49]

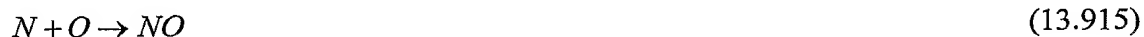
$$15 \quad E_{D298}(CO) = 11.15696 \text{ eV} \quad (13.914)$$

The results of the determination of bond parameters of  $CO$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

5

## NITRIC OXIDE RADICAL

The nitric oxide radical can be formed by the reaction of nitrogen and oxygen atoms:

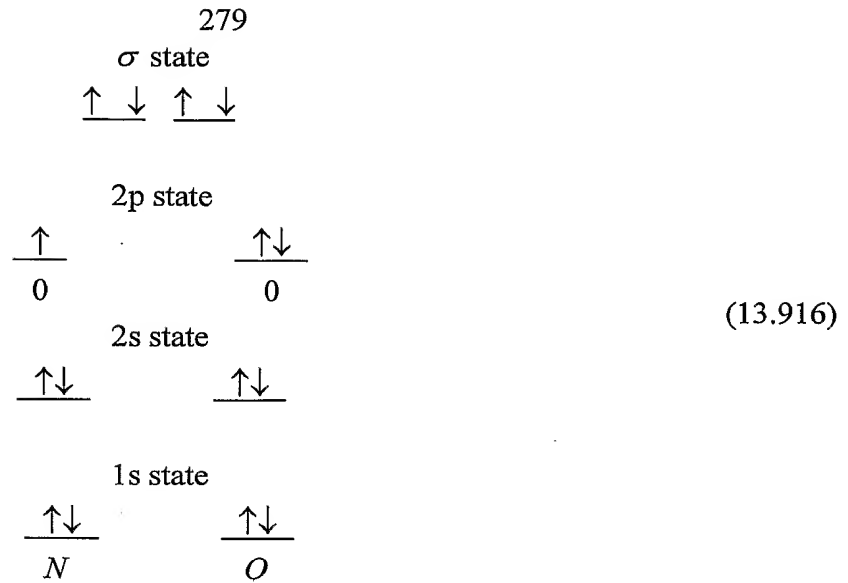


The bond in the nitric oxide radical comprises a double bond, a  $H_2$ -type molecular orbital (MO) with four paired electrons. The force balance equation and radius  $r_7$  of the  $2p$  shell of  $N$  is derived in the Seven-Electron Atoms section. The force balance equation and radius  $r_8$  of the  $2p$  shell of  $O$  is derived in the Eight-Electron Atoms section. With the formation of the  $H_2$ -type MO by the contribution of two  $2p$  electrons from each of the  $N$  and  $O$  atoms, a diamagnetic force arises between the remaining outer shell atomic electrons, the  $2s$  and  $2p$  electrons of  $N$  and  $O$ , and the  $H_2$ -type MO. This force from  $N$  and  $O$  causes the  $H_2$ -type MO to move to greater principal axes than would result with the Coulombic force alone. But, the factor of two increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining  $N$  and  $O$  electrons decrease the radii of the corresponding shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of  $NO$  is  $N1s^2O1s^2N2s^2O2s^2N2p^1O2p^2\sigma_{N,O}^4$  where  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is

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Nitric oxide is predicted to be weakly paramagnetic in agreement with observations [42].

## FORCE BALANCE OF THE $2p$ SHELL OF THE NITROGEN ATOM OF 5 THE NITRIC OXIDE RADICAL

For the  $N$  atom, force balance for the outermost  $2p$  electron of  $NO$  (electron 5) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 5 and the  $2s$ -shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central  
10 Coulomb force on the outer-most  $2p$  shell electron of  $NO$  (electron 5) due to the nucleus and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\epsilon_0 r_5^2} \mathbf{i}_r \quad (13.917)$$

for  $r > r_4$ . The  $2p$  shell possess a +2 external electric field given by Eq. (10.92) for  $r > r_5$ .

The energy is minimized with conservation of angular momentum. This condition is met  
15 when the magnetic forces of  $N$  in  $NO$  are the same as those of  $N$  in the nitrogen molecule with  $r_5$  replacing  $r_6$  and with an increase of the central field by an integer. The diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the  $p$ -orbital contribution is given by Eq. (13.622) with  $r_5$  replacing  $r_6$ :

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right) \frac{\hbar^2}{4m_e r_5^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{\hbar^2}{12m_e r_5^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r \quad (13.918)$$

20 And,  $\mathbf{F}_{mag\ 2}$  corresponding to the conserved orbital angular momentum of the three orbitals is

also the same as that of  $N_2$  given by Eq. (13.623) with  $r_5$  replacing  $r_6$ :

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{3\hbar^2}{m_e r_5^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (13.919)$$

The electric field external to the  $2p$  shell given by Eq. (10.92) for  $r > r_5$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +2 outside of its radius follows from Eq. (13.624):

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_5^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (13.920)$$

In addition to the  $N$  forces  $\mathbf{F}_{ele}$ ,  $\mathbf{F}_{diamagnetic}$ ,  $\mathbf{F}_{mag\ 2}$ , and  $\mathbf{F}_{diamagnetic\ 2}$  of  $NO$  being the same as  $N_2$  given by Eqs. (13.621-13.624), respectively,  $\mathbf{F}_{ele}$ ,  $\mathbf{F}_{mag\ 2}$ , and  $\mathbf{F}_{diamagnetic\ 2}$  are also the same as those of  $CN$  (Eqs. (13.820) and (13.822-13.823)). In the  $N_2$  and  $CN$  cases, the contribution of a  $2p$  electron from the  $N$  atom in the formation of the  $\sigma$  MO gives rise to an additional paramagnetic force on the remaining two  $2p$  electrons that pair. However, the force,  $\mathbf{F}_{mag\ 3}$ , is absent in  $NO$  since the single outer electron is unpaired.

The radius of the  $2p$  shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.917)) and diamagnetic (Eqs. (13.918) and (13.920)), and paramagnetic (Eq. (13.919)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \left[ \frac{(Z-4)e^2}{4\pi\epsilon_0 r_5^2} - \frac{\hbar^2}{12m_e r_5^2 r_3} \sqrt{s(s+1)} + \frac{3\hbar^2}{Zm_e r_5^2 r_3} \sqrt{s(s+1)} - \left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_5^4 m_e} 10 \sqrt{s(s+1)} \right] \quad (13.921)$$

Substitution of  $v_5 = \frac{\hbar}{m_e r_5}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.921) gives:

$$\frac{\hbar^2}{m_e r_5^3} = \frac{(Z-4)e^2}{4\pi\epsilon_0 r_5^2} - \frac{\hbar^2}{12m_e r_5^2 r_3} \sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Zm_e r_5^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_5^4 m_e} 10 \sqrt{\frac{3}{4}} \quad (13.922)$$

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The quadratic equation corresponding to Eq. (13.922) is



$$r_5^2 - \frac{\frac{\hbar^2}{m_e}}{\left( \frac{(Z-4)e^2}{4\pi\epsilon_0} - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} r_5 - \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-5}{Z-4} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-4)e^2}{4\pi\epsilon_0} - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} = 0 \quad (13.923)$$

The solution of Eq. (13.923) using the quadratic formula is:

$$r_5 = \frac{\frac{a_0}{\left( (Z-4) - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)} \pm a_0}{2} \pm \frac{\sqrt{\left( \frac{1}{\left( (Z-4) - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)} \right)^2 + \frac{20\sqrt{3} \left[ \frac{Z-5}{Z-4} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3}{\left( (Z-4) - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)}}}{2} \quad (13.924)$$

$r_3$  in units of  $a_0$

5 The positive root of Eq. (13.924) must be taken in order that  $r_5 > 0$ . Substitution of

$\frac{r_3}{a_0} = 0.69385$  (Eq. (10.62) with  $Z = 7$ ) into Eq. (13.924) gives

$$r_5 = 0.74841 a_0 \quad (13.925)$$

## FORCE BALANCE OF THE 2p SHELL OF THE OXYGEN ATOM OF THE 10 NITRIC OXIDE RADICAL

For the O atom, force balance for the outermost 2p electron of NO (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other 2p electron as well as the 2s-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron  
15 Atoms section. The central Coulomb force on the outer-most 2p shell electron of NO (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} \mathbf{i}_r \quad (13.926)$$

for  $r > r_5$ . The  $2p$  shell possess an external electric field of +2 given by Eq. (10.92) for  $r > r_6$ . The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force,  $\mathbf{F}_{\text{diamagnetic}}$ , of Eq. (10.82) due to the  $p$ -orbital contribution is given by:

$$5 \quad \mathbf{F}_{\text{diamagnetic}} = -\left(\frac{2}{3}\right) \frac{\hbar^2}{4m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r \quad (13.927)$$

And,  $\mathbf{F}_{\text{mag } 2}$  corresponding to the conserved spin and orbital angular momentum given by Eqs. (10.157) and (13.670) is

$$\mathbf{F}_{\text{mag } 2} = \frac{1}{Z} \frac{2\hbar^2}{m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (13.928)$$

The electric field external to the  $2p$  shell given by Eq. (10.92) for  $r > r_6$  gives rise to  
10 a second diamagnetic force,  $\mathbf{F}_{\text{diamagnetic } 2}$ , given by Eq. (10.93).  $\mathbf{F}_{\text{diamagnetic } 2}$  due to the binding of the  $p$ -orbital electron having an electric field of +2 outside of its radius is :

$$\mathbf{F}_{\text{diamagnetic } 2} = -\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (13.929)$$

In addition, the contribution of two  $2p$  electrons in the formation of the  $\sigma$  MO gives rise to a paramagnetic force on the remaining paired  $2p$  electrons. The force  $\mathbf{F}_{\text{mag } 3}$  is given  
15 by Eq. (13.625) wherein the radius is  $r_6$  :

$$\mathbf{F}_{\text{mag } 3} = \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \mathbf{i}_r \quad (13.930)$$

The radius of the  $2p$  shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.926)) and diamagnetic (Eqs. (13.927) and (13.929)), and paramagnetic (Eqs. (13.928) and (13.930)) forces as follows:

$$20 \quad \frac{m_e v_6^2}{r_6} = \left( \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{s(s+1)} \right. \\ \left. - \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \right) \quad (13.931)$$

Substitution of  $v_6 = \frac{\hbar}{m_e r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.931) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3} \sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{\frac{3}{4}} - \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{\frac{3}{4}}$$

(13.932)

The quadratic equation corresponding to Eq. (13.932) is

$$r_6^2 - \frac{\frac{\hbar^2}{m_e} \left(1 - \frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-5)e^2}{4\pi\epsilon_0} - \left(\frac{2}{12} - \frac{2}{Z}\right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)} r_6 - \frac{\frac{\hbar^2}{m_e} \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) r_3 10 \sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\epsilon_0} - \left(\frac{2}{12} - \frac{2}{Z}\right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}}\right)} = 0 \quad (13.933)$$

The solution of Eq. (13.933) using the quadratic formula is:

$$r_6 = \frac{a_0 \left(1 - \frac{\sqrt{3}}{8}\right)}{\left((Z-5) - \left(\frac{2}{12} - \frac{2}{Z}\right) \frac{\sqrt{3}}{2r_3}\right)} \pm a_0 \sqrt{\frac{\left(\frac{1 - \frac{\sqrt{3}}{8}}{\left((Z-5) - \left(\frac{2}{12} - \frac{2}{Z}\right) \frac{\sqrt{3}}{2r_3}\right)}\right)^2 - 20\sqrt{3} \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) r_3}{\left((Z-5) - \left(\frac{2}{12} - \frac{2}{Z}\right) \frac{\sqrt{3}}{2r_3}\right)^2}} \quad (13.934)$$

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$r_3$  in units of  $a_0$

The positive root of Eq. (13.934) must be taken in order that  $r_6 > 0$ . Substitution of

$\frac{r_3}{a_0} = 0.59020$  (Eq. (10.62) with  $Z = 8$ ) into Eq. (13.934) gives

$$r_6 = 0.70460 a_0 \quad (13.935)$$

## 10 ENERGIES OF THE $2p$ SHELLS OF THE NITROGEN ATOM AND OXYGEN ATOM OF THE NITRIC OXIDE RADICAL

With the formation of the  $H_2$ -type MO by the contribution of two  $2p$  electrons from each of the  $N$  and  $O$  atoms, the total energy of the  $NO$  molecule, which is subtracted from the sum of the energies of the nitrogen and oxygen atoms to determine the bond energy, is increased by the ionization energies of  $N^+$  and  $O^+$  given by Eqs. (10.132-10.133) and (10.152-10.153), respectively. Experimentally, the energies are [6]

$$E(\text{ionization}; N^+) = 29.6013 \text{ eV} \quad (13.936)$$

$$E(\text{ionization}; O^+) = 35.11730 \text{ eV} \quad (13.937)$$

In addition, the central forces on the  $2p$  shells of the  $N$  and  $O$  atoms are increased

with the formation of the  $\sigma$  MO which reduces each shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the  $N$  and  $O$  atoms at the new radii are calculated and added to the ionization energies of  $N^+$  and  $O^+$ , and the energy of the  $\sigma$  MO to give the total energy of  $NO$ . Then, the bond energy is determined from the total  $NO$  energy.

The radius  $r_7$  of the nitrogen atom before bonding is given by Eq. (10.142):

$$r_7 = 0.93084a_0 \quad (13.938)$$

Using the initial radius  $r_7$  of the  $N$  atom and the final radius  $r_5$  of the  $N2p$  shell (Eq. (13.925)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(N, 2p)$  of the Coulombic energy change of the  $N2p$  electrons of the  $N$  atom is determined using Eq. (10.102):

$$\begin{aligned} E_T(N, 2p) &= -\sum_{n=4}^4 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_5} - \frac{1}{r_7} \right) \\ &= -(13.60580 \text{ eV})(0.26186)(3) \\ &= -10.68853 \text{ eV} \end{aligned} \quad (13.939)$$

The radius  $r_8$  of the oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 \quad (13.940)$$

Using the initial radius  $r_8$  of the  $O$  atom and the final radius  $r_6$  of the  $O2p$  shell (Eq. (13.935)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(O, 2p)$  of the Coulombic energy change of the  $O2p$  electrons of the  $O$  atom is determined using Eq. (10.102):

$$\begin{aligned} E_T(O, 2p) &= -\sum_{n=4}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_8} \right) \\ &= -(13.60580 \text{ eV})(0.41925)(3+4) \\ &= -39.92918 \text{ eV} \end{aligned} \quad (13.941)$$

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## FORCE BALANCE OF THE $\sigma$ MO OF THE NITRIC OXIDE RADICAL

The force balance can be considered due to a second pair of two electrons binding to a molecular ion having  $+2e$  at each focus and a first bound pair. Then, the forces are the same as those of a molecule ion having  $+e$  at each focus. The diamagnetic force  $F_{\text{diamagneticMO1}}$  for the  $\sigma$ -MO of the  $NO$  molecule due to the two paired electrons in the  $O2p$  shell is given by

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Eq. (13.633) with  $n_e = 2$ :

$$\mathbf{F}_{\text{diamagneticMO1}} = \frac{\hbar^2}{2m_e a^2 b^2} D \mathbf{i}_\xi \quad (13.942)$$

$\mathbf{F}_{\text{diamagneticMO2}}$  of the nitric oxide radical comprising nitrogen with charge  $Z_1 = 7$  and  $|L_1| = \hbar$  and  $|L_2| = \sqrt{\frac{3}{4}}\hbar$  and oxygen with  $Z_2 = 8$  and  $|L_3| = \hbar$  is given by the corresponding sum of the

5 contributions. Using Eq. (13.835),  $\mathbf{F}_{\text{diamagneticMO2}}$  for NO is

$$\mathbf{F}_{\text{diamagneticMO2}} = \left( \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D \mathbf{i}_\xi \quad (13.943)$$

The general force balance equation for the  $\sigma$ -MO of the nitric oxide radical given by Eqs. (11.200), (13.633-13.634), and (13.942-13.943) is the same as that of CN (Eq. (13.836)):

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left( 1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.944)$$

$$10 \quad \frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 ab^2} D - \left( \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.945)$$

$$\left( 2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 ab^2} D \quad (13.946)$$

$$a = \left( 2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) a_0 \quad (13.947)$$

Substitution of  $Z_1 = 7$  and  $Z_2 = 8$  into Eq. (13.947) gives

$$a = 2.39158a_0 = 1.26557 \times 10^{-10} \text{ m} \quad (13.948)$$

15 Substitution of Eq. (13.948) into Eq. (11.79) is

$$c' = 1.09352a_0 = 5.78666 \times 10^{-11} \text{ m} \quad (13.949)$$

The internuclear distance given by multiplying Eq. (13.949) by two is

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$$2c' = 2.18704a_0 = 1.15733 \times 10^{-10} \text{ m} \quad (13.950)$$

The experimental bond distance is [28]

$$2c' = 1.15077 \times 10^{-10} \text{ m} \quad (13.951)$$

Substitution of Eqs. (13.948-13.949) into Eq. (11.80) is

$$5 \quad b = c = 2.12693a_0 = 1.12552 \times 10^{-10} \text{ m} \quad (13.952)$$

Substitution of Eqs. (13.948-13.949) into Eq. (11.67) is

$$e = 0.45724 \quad (13.953)$$

Using the electron configuration of *NO* (Eq. (13.916)), the radii of the *N*1*s* = 0.14605*a*<sub>0</sub> (Eq. (10.51)), *N*2*s* = 0.69385*a*<sub>0</sub> (Eq. (10.62)), *N*2*p* = 0.74841*a*<sub>0</sub> (Eq. (13.925)), *O*1*s* = 0.12739*a*<sub>0</sub> (Eq. (10.51)), *O*2*s* = 0.59020*a*<sub>0</sub> (Eq. (10.62)), and *O*2*p* = 0.70460*a*<sub>0</sub> (Eq. (13.935)) shells and the parameters of the  $\sigma$  MO of *NO* given by Eqs. (13.3-13.4), (13.948-13.950), and (13.952-13.953), the dimensional diagram and charge-density of the *NO* MO are shown in Figures 31 and 32, respectively.

## 15 SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE NITRIC OXIDE RADICAL

The energies of the *NO*  $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. (13.948-13.949) and (13.952)) into the energy equations (Eqs. (11.207-11.212)) of *H*<sub>2</sub> except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the  $\sigma$ -MO double bond with two pairs of paired electrons:

$$V_e = 2^2 \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -98.30623 \text{ eV} \quad (13.954)$$

$$V_p = 2^2 \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 49.76880 \text{ eV} \quad (13.955)$$

$$T = 2 \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 10.27631 \text{ eV} \quad (13.956)$$

$$V_m = 2^2 \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -10.27631 \text{ eV} \quad (13.957)$$

$$25 \quad E_T = V_e + T + V_m + V_p \quad (13.958)$$

Substitution of Eqs. (11.79) and (13.954-13.957) into Eq. (13.958) gives

$$E_T(NO, \sigma) = \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left( \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 4 \right) = -48.53743 \text{ eV} \quad (13.959)$$

where  $E_T(NO, \sigma)$  is the total energy of the  $\sigma$  MO of  $NO$ . The total energy of  $NO$ ,  $E_T(NO)$ , is given by the sum of  $E(\text{ionization}; N^+)$ , the energy of the second electron of nitrogen (Eq. (13.936)) donated to the double bond,  $E(\text{ionization}; O^+)$ , the energy of the second electron of oxygen (Eq. (13.937)) donated to the double bond,  $E_T(N, 2p)$ , the  $N2p$  AO contribution due to the decrease in radius with bond formation (Eq. (13.939)),  $E_T(O, 2p)$ , the  $O2p$  AO contribution due to the decrease in radius with bond formation (Eq. (13.941)), and  $E_T(NO, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (13.959):

$$\begin{aligned} E_T(NO) &= \left( E(\text{ionization}; N^+) + E(\text{ionization}; O^+) \right) \\ &\quad + E_T(N, 2p) + E_T(O, 2p) + E_T(NO, \sigma) \\ &= \left( 29.6013 \text{ eV} + 35.11730 \text{ eV} \right. \\ &\quad \left. - 10.68853 \text{ eV} - 39.92918 \text{ eV} - 48.53743 \text{ eV} \right) \\ &= -34.43653 \text{ eV} \end{aligned} \quad (13.960)$$

10

## VIBRATION OF $NO$

The vibrational energy levels of  $NO$  may be solved by determining the Morse potential curve from the energy relationships for the transition from a  $N$  atom and  $O$  atom whose parameters are given by Eqs. (10.134-10.143) and (10.154-10.163), respectively, to a  $N$  atom whose parameter  $r_s$  is given by Eq. (13.925), an  $O$  atom whose parameter  $r_e$  is given by Eq. (13.935), and the  $\sigma$  MO whose parameters are given by Eqs. (13.948-13.950) and (13.952-13.953). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

20

## THE DOPPLER ENERGY TERMS OF THE NITRIC OXIDE RADICAL

The equations of the radiation reaction force of nitric oxide are the same as those of  $H_2$  with the substitution of the  $NO$  parameters except that there is a factor of four increase in the central force in Eq. (11.231) due to the double bond. Using Eqs. (11.231-11.233) and  
 5 (13.901), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{4e^2}{4\pi\epsilon_0 a^3}} = 2.23557 \times 10^{16} \text{ rad/s} \quad (13.961)$$

where  $a$  is given by Eq. (13.948). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.23557 \times 10^{16} \text{ rad/s} = 14.71493 \text{ eV} \quad (13.962)$$

10 In Eq. (11.181), substitution of  $E_T(NO)$  for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (13.962) for  $\bar{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -34.43653 \text{ eV} \sqrt{\frac{2e(14.71493 \text{ eV})}{m_e c^2}} = -0.26134 \text{ eV} \quad (13.963)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the  
 15 transition state at their corresponding frequency. The decrease in the energy of the  $NO$  MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (13.963) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental  $NO$   $\omega_e$  of  $1904.20 \text{ cm}^{-1}$  ( $0.23609 \text{ eV}$ ) [28] for

20  $\bar{E}_{Kvib}$  of the transition state,  $\bar{E}'_{osc}(NO)$  per bond is

$$\bar{E}'_{osc}(NO) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (13.964)$$

$$\bar{E}'_{osc}(NO) = -0.26134 \text{ eV} + \frac{1}{2} (0.23609 \text{ eV}) = -0.14329 \text{ eV} \quad (13.965)$$

Since the  $\sigma$  MO bond is a double bond with twice as many electrons as a single bond,  $\bar{E}'_{osc}(NO)$  is multiplied by two to give

$$25 \quad \bar{E}_{osc}(NO) = -0.28658 \text{ eV} \quad (13.966)$$



## TOTAL AND BOND ENERGIES OF THE NITRIC OXIDE RADICAL

$E_{T+osc}(NO)$ , the total energy of  $NO$  including the Doppler term, is given by the sum of  $E_T(NO)$  (Eq. (13.960)) and  $\bar{E}_{osc}(NO)$  given by Eq. (13.966):

$$\begin{aligned}
 E_{T+osc}(NO) &= \left( V_e + T + V_m + V_p + E(\text{ionization}; N^+) + E(\text{ionization}; O^+) \right) \\
 &\quad + E_T(N, 2p) + E_T(O, 2p) + \bar{E}_{osc}(NO) \\
 &= \left( E_T(NO, \sigma) + E(\text{ionization}; N^+) + E(\text{ionization}; O^+) \right) \\
 &\quad + E_T(N, 2p) + E_T(O, 2p) + \bar{E}_{osc}(NO) \\
 &= E_T(NO) + \bar{E}_{osc}(NO)
 \end{aligned} \tag{13.967}$$

$$\begin{aligned}
 E_{T+osc}(NO) &= \left\{ \begin{aligned} &\frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left( \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 4 \right) \\ &+ E(\text{ionization}; N^+) + E(\text{ionization}; O^+) \\ &- \sum_{N,n=4}^4 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_5} - \frac{1}{r_7} \right) - \sum_{O,n=4}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_8} \right) \\ &\left( 1 + 2\sqrt{\frac{2\hbar\sqrt{\frac{4e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} \right) + 2\left( \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right) \end{aligned} \right\} \\
 &= -34.43653 \text{ eV} - 2(0.26134 \text{ eV}) + 2\left( \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right)
 \end{aligned} \tag{13.968}$$

From Eqs. (13.966-13.968), the total energy of the  $NO$  MO is

$$\begin{aligned}
 E_{T+osc}(NO) &= -34.43653 \text{ eV} + \bar{E}_{osc}(NO) \\
 &= -34.43653 \text{ eV} + (-0.28658) \\
 &= -34.72312 \text{ eV}
 \end{aligned} \tag{13.969}$$

where the experimental  $\omega_e$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

10 The  $NO$  bond dissociation energy,  $E_D(NO)$ , is given by the difference between the sum of the energies of the  $N$  and  $O$  atoms and  $E_{T+osc}(NO)$ :

$$E_D(NO) = E(N) + E(O) - E_{T+osc}(NO) \tag{13.970}$$

where the energy of a nitrogen atom is [6]

$$E(N) = -14.53414 \text{ eV} \quad (13.871)$$

and the energy of an oxygen atom is [6]

$$E(O) = -13.61806 \text{ eV} \quad (13.972)$$

Thus, the  $NO$  bond dissociation energy,  $E_D(NO)$ , given by Eqs. (13.969-13.972) is

$$\begin{aligned} E_D(NO) &= -(14.53414 \text{ eV} + 13.61806 \text{ eV}) - E_{T+osc}(NO) \\ &= -28.15220 \text{ eV} - (-34.72312 \text{ eV}) \\ &= 6.57092 \text{ eV} \end{aligned} \quad (13.973)$$

The experimental  $NO$  bond dissociation energy is [49]

$$E_{D298}(NO) = 6.5353 \text{ eV} \quad (13.974)$$

The results of the determination of bond parameters of  $NO$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

Table 13.1. The calculated and experimental bond parameters of  $H_3^+$ ,  $D_3^+$ ,  $OH$ ,  $OD$ ,  $H_2O$ ,  $D_2O$ ,  $NH$ ,  $ND$ ,  $NH_2$ ,  $ND_2$ ,  $NH_3$ ,  $ND_3$ ,  $CH$ ,  $CD$ ,  $CH_2$ ,  $CH_3$ ,  $CH_4$ ,  $N_2$ ,  $O_2$ ,  $F_2$ ,  $Cl_2$ ,  $CN$ ,  $CO$ , and  $NO$ .

Parameter	Calculated	Experimental	Ref. for Exp.
$H_3^+$ Bond Energy	4.373 eV	4.373 eV	8
$D_3^+$ Bond Energy	4.374 eV		
$OH$ Bond Energy	4.4104 eV	4.4117 eV	22
$OD$ Bond Energy	4.4687 eV	4.454 eV	23
$OH$ Bond Length	0.971651 Å	0.971 Å	13
$OD$ Bond Length	0.971651 Å	0.971 Å	13
$OH$ Vibrational Energy	0.4367 eV	0.4424 eV	16-17
$OD$ Vibrational Energy	0.3219 eV	0.3263 eV	16-17
$OH$ $\omega_e$	3696.38 $cm^{-1}$	3735.21 $cm^{-1}$	14
$OD$ $\omega_e$	2689.51 $cm^{-1}$	2720.9 $cm^{-1}$	14
$OH$ $\omega_e x_e$	87.18 $cm^{-1}$	82.81 $cm^{-1}$	14
$OD$ $\omega_e x_e$	46.75 $cm^{-1}$	44.2 $cm^{-1}$	14
$OH$ $B_e$	18.835 $cm^{-1}$	18.871 $cm^{-1}$	14

Parameter	291		
	Calculated	Experimental	Ref. for Exp.
$OD\ B_e$	$9.971\text{ cm}^{-1}$	$10.01\text{ cm}^{-1}$	14
$H_2O$ Bond Energy	5.1059 eV	5.0991 eV	26
$D_2O$ Bond Energy	5.178 eV	5.191 eV	31-32
$H_2O$ $O-H$ Bond Length	$0.971574\text{ Å}$	$0.970 \pm 0.005\text{ Å}$	23
$D_2O$ $O-D$ Bond Length	$0.971574\text{ Å}$	$0.970 \pm 0.005\text{ Å}$	23
$H_2O$ $H-H$ Distance	$1.552\text{ Å}$	$1.55 \pm 0.01\text{ Å}$	13
$D_2O$ $D-D$ Distance	$1.552\text{ Å}$	$1.55 \pm 0.01\text{ Å}$	13
$H_2O$ Bond Angle	$106^\circ$	$106^\circ$	23
$D_2O$ Bond Angle	$106^\circ$	$106^\circ$	23
$NH$ Bond Energy	3.47530 eV	3.47 eV	30
$ND$ Bond Energy	3.52556 eV	3.5134 eV	31
$NH$ Bond Length	$1.04262\text{ Å}$	$1.0362\text{ Å}$	28
$ND$ Bond Length	$1.04262\text{ Å}$	$1.0361\text{ Å}$	28
$NH$ Vibrational Energy	0.38581 eV	0.38752 eV	28
$ND$ Vibrational Energy	0.28583 eV	0.28690 eV	28
$NH\ \omega_e$	$3284.58\text{ cm}^{-1}$	$3282.3\text{ cm}^{-1}$	28
$ND\ \omega_e$	$2398.72\text{ cm}^{-1}$	$2398\text{ cm}^{-1}$	28
$NH\ \omega_e x_e$	$86.37\text{ cm}^{-1}$	$78.4\text{ cm}^{-1}$	28
$ND\ \omega_e x_e$	$47.40\text{ cm}^{-1}$	$42\text{ cm}^{-1}$	28
$NH\ B_e$	$16.495\text{ cm}^{-1}$	$16.993\text{ cm}^{-1}$	28
$ND\ B_e$	$8.797\text{ cm}^{-1}$	$8.7913\text{ cm}^{-1}$	28
$NH_2$ Bond Energy	3.9323 eV	3.9461 eV	35
$ND_2$ Bond Energy	3.9401 eV	3.9362 eV	33-35
$NH_2$ Bond Length	$1.04262\text{ Å}$	$1.0240\text{ Å}$	32
$ND_2$ Bond Length	$1.04262\text{ Å}$		
$NH_2$ Bond Angle	105.97	$103.3^\circ$	32
$ND_2$ Bond Angle	105.97		
$NH_3$ Bond Energy	4.57913 eV	4.60155 eV	37
$ND_3$ Bond Energy	4.64499 eV	4.71252 eV	37

Parameter	292		
	Calculated	Experimental	Ref. for Exp.
$NH_3$ Bond Length	1.0368 Å	1.012 Å	32
$ND_3$ Bond Length	1.0368 Å		
$NH_3$ Bond Angle	106.67	106.67°	36
$ND_3$ Bond Angle	106.67	106.70	36
$CH$ Bond Energy	3.47404 eV	3.47 eV	14
$CD$ Bond Energy	3.51673 eV	3.52 eV	14
$CH$ Bond Length	1.1183 Å	1.1198 Å	14
$CD$ Bond Length	1.1183 Å	1.118 Å	14
$CH$ Vibrational Energy	0.33879 eV	0.33885 eV	14
$CD$ Vibrational Energy	0.25173 eV	0.25189 eV	14
$CH$ $\omega_e$	2865.86 $cm^{-1}$	2861.6 $cm^{-1}$	14
$CD$ $\omega_e$	2102.97 $cm^{-1}$	2101.0 $cm^{-1}$	14
$CH$ $\omega_e x_e$	66.624 $cm^{-1}$	64.3 $cm^{-1}$	14
$CD$ $\omega_e x_e$	36.335 $cm^{-1}$	34.7 $cm^{-1}$	14
$CH$ $B_e$	14.498 $cm^{-1}$	14.457 $cm^{-1}$	14
$CD$ $B_e$	7.807 $cm^{-1}$	7.808 $cm^{-1}$	14
$CH_2$ Bond Energy	4.36968 eV	4.33064 eV	39
$CH_2$ Bond Length	1.1067 Å	1.111 Å	38
$CH_2$ Bond Angle	100.22	102.4°	38
$CH_3$ Bond Energy	4.70075 eV	4.72444 eV	40
$CH_3$ Bond Length	1.1029 Å	1.079 Å	38
$CH_3$ Bond Angle	100.70°		
$CH_4$ Bond Energy	4.4900 eV	4.48464 eV	40
$CH_4$ Bond Length	1.1010 Å	1.087 Å	41
$CH_4$ Bond Angle	109.5°	109.5°	41
$N_2$ Bond Energy	9.71181 eV	9.756 eV	43
$N_2$ Bond Length	1.0955 Å	1.094 Å	43
$O_2$ Bond Energy	5.10711 eV	5.11665 eV	46
$O_2$ Bond Length	1.20862 Å	1.20752 Å	28

Parameter	293		
	Calculated	Experimental	Ref. for Exp.
$F_2$ Bond Energy	1.62168 eV	1.606 eV	48
$F_2$ Bond Length	1.41114 Å	1.41193 Å	28
$Cl_2$ Bond Energy	2.52236 eV	2.51412 eV	49
$Cl_2$ Bond Length	1.988 Å	1.988 Å	28
$Cl_2$ $\omega_e$	538.52 $cm^{-1}$	559.7 $cm^{-1}$	28
$Cl_2$ $\omega_e x_e$	3.41 $cm^{-1}$	2.68 $cm^{-1}$	28
$Cl_2$ $B_e$	0.2420 $cm^{-1}$	0.2440 $cm^{-1}$	28
CN Bond Energy	7.77526 eV	7.7731 eV	50
CN Bond Length	1.17231 Å	1.17181 Å	28
CO Bond Energy	11.16652 eV	11.15696 eV	49
CO Bond Length	1.13290 Å	1.12823 Å	28
NO Bond Energy	6.57092 eV	6.5353 eV	49
NO Bond Length	1.15733 Å	1.15077 Å	28

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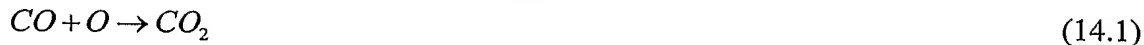
## Section III

### MORE POLYATOMIC MOLECULES AND HYDROCARBONS

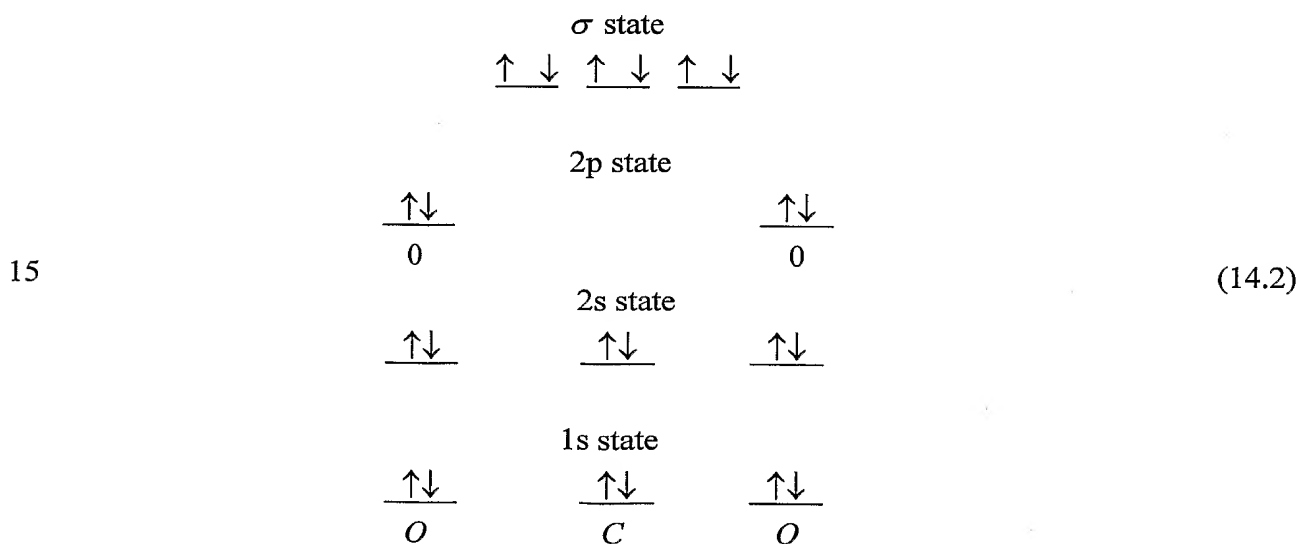
Additional polyatomic molecules can be solved using the same principles as those used to  
 5 solve hydrogen molecular ions and molecules wherein the hydrogen molecular orbitals (MOs)  
 and hydrogen atomic orbitals serve as basis functions for the MOs. The MO must (1) be a  
 solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an  
 orbital solution of the Newtonian equation of motion in an inverse-radius-squared central  
 field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron  
 10 angular momentum of  $\hbar$ . Energy of the MO must be matched to that of the outermost atomic  
 orbital of a bonding heteroatom in the case where a minimum energy is achieved with a direct  
 bond to the AO. Alternatively, the MO is continuous with the AO containing paired electrons  
 that do not participate in the bond. Rather, they only provide a means for the energy matched  
 MO to form a continuous equipotential energy surface. In the case that an independent MO is  
 15 formed, the AO force balance causes the remaining electrons to be at lower energy and a  
 smaller radius. In another case, the atomic orbital may hybridize in order to achieve a bond at  
 an energy minimum, and the sharing of electrons between two or more such orbitals to form a  
 MO permits the participating hybridized orbitals to decrease in energy through a decrease in  
 the radius of one or more of the participating orbitals. Representative cases were solved.  
 20 Specifically, the results of the determination of bond parameters of carbon dioxide ( $CO_2$ ),  
 nitrogen dioxide ( $NO_2$ ), ethane ( $CH_3CH_3$ ), ethylene ( $CH_2CH_2$ ), acetylene ( $CHCH$ ),  
 benzene ( $C_6H_6$ ), propane ( $C_3H_8$ ), butane ( $C_4H_{10}$ ), pentane ( $C_5H_{12}$ ), hexane ( $C_6H_{14}$ ),  
 heptane ( $C_7H_{16}$ ), octane ( $C_8H_{18}$ ), nonane ( $C_9H_{20}$ ), decane ( $C_{10}H_{22}$ ), undecane ( $C_{11}H_{24}$ ),  
 dodecane ( $C_{12}H_{26}$ ), and octadecane ( $C_{18}H_{38}$ ) are given in Table 14.1. The calculated results  
 25 are based on first principles and given in closed-form, exact equations containing  
 fundamental constants only. The agreement between the experimental and calculated results  
 is excellent.

#### CARBON DIOXIDE MOLECULE

30 The carbon dioxide molecule can be formed by the reaction of carbon monoxide and an  
 oxygen atom:



Each equivalent bond in the carbon dioxide molecule comprises a double bond that is energy-matched to the filled  $C2s$  orbital. Each such bond comprises 75% of a  $H_2$ -type MO with four paired electrons as a basis set such that three electrons can be assigned to each  $C=O$  bond. Thus, the two  $C2p$  electrons combine with the four  $O2p$  electrons, two from each  $O$ , as a linear combination to form the two  $C=O$  bonds of  $CO_2$ . The force balance equation and radius  $r_8$  of the  $2p$  shell of  $O$  is derived in the Eight-Electron Atoms section. With the formation of the  $H_2$ -type MOs by the contribution of two  $2p$  electrons from each of the two  $O$  atoms, a factor of two increase of the central field on the remaining  $O2p$  electrons arises. The resulting increased Coulombic as well as magnetic central forces decrease the radii of the  $O2p$  shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of  $CO_2$  is  $C1s^2O_11s^2O_21s^2C2s^2O_12s^2O_22s^2O_12p^2O_22p^2\sigma_{O_2,C,O_1}^6$  where the subscripts designate the  $O$  atom, 1 or 2,  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is



Carbon dioxide is predicted to be diamagnetic in agreement with observations [1].

#### FORCE BALANCE OF THE $2p$ SHELL OF THE OXYGEN ATOM OF THE CARBON DIOXIDE MOLECULE

For each  $O$  atom, force balance for the outermost  $2p$  electron of  $CO_2$  (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due

to interactions between electron 6 and the other  $2p$  electrons as well as the  $2s$ -shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most  $2p$  shell electron of  $CO$  (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} \mathbf{i}_r \quad (14.3)$$

for  $r > r_5$ . The  $2p$  shell possess a +2 external electric field given by Eq. (10.92) for  $r > r_6$ . The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the  $p$ -orbital contribution is

10 given by:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right) \frac{\hbar^2}{4m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r \quad (14.4)$$

where  $s=1/2$ . And,  $\mathbf{F}_{mag\ 2}$  corresponding to the conserved spin and orbital angular momentum given by Eq. (10.157) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{2\hbar^2}{m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (14.5)$$

15 The electric field external to the  $2p$  shell given by Eq. (10.92) for  $r > r_6$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the  $p$ -orbital electron having an electric field of +2 outside of its radius is :

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (14.6)$$

The radius of the  $2p$  shell is calculated by equating the outward centrifugal force to 20 the sum of the electric (Eq. (14.3)) and diamagnetic (Eqs. (14.4) and (14.6)), and paramagnetic (Eq. (14.5)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{s(s+1)} - \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{s(s+1)} \quad (14.7)$$

Substitution of  $v_6 = \frac{\hbar}{m_e r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (14.7) gives:

$$\frac{\hbar^2}{m_e r_6^3} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{\frac{3}{4}} - \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{\frac{3}{4}} \quad (14.8)$$

The quadratic equation corresponding to Eq. (14.8) is

$$r_6^2 - \frac{\frac{\hbar^2}{m_e}}{\left( \frac{(Z-5)e^2}{4\pi\epsilon_0} - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} r_6 - \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-5)e^2}{4\pi\epsilon_0} - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} = 0 \quad (14.9)$$

5 The solution of Eq. (14.9) using the quadratic formula is:

$$r_6 = \frac{\frac{a_0}{\left( (Z-5) - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)} \pm a_0}{2} \sqrt{\frac{1}{\left( (Z-5) - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)^2} + \frac{20\sqrt{3} \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3}{\left( (Z-5) - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)}} \quad (14.10)$$

$r_3$  in units of  $a_0$

The positive root of Eq. (14.10) must be taken in order that  $r_6 > 0$ . Substitution of

$\frac{r_3}{a_0} = 0.59020$  (Eq. (10.62) with  $Z = 8$ ) into Eq. (14.10) gives

$$r_6 = 0.74776a_0 \quad (14.11)$$

10

## ENERGIES OF THE $2s$ AND $2p$ SHELLS OF THE CARBON ATOM AND THE $2p$ SHELL OF THE OXYGEN ATOMS OF THE CARBON DIOXIDE MOLECULE

Consider the determination of the total energy of  $CO_2$  from the reaction of a carbon atom  
 15 with two oxygen atoms. With the formation of the  $H_2$ -type MO by the contribution of two  $2p$  electrons from the  $C$  atom, the remaining outer-shell atomic electrons comprise the  $2s$  electrons which are unchanged by bonding with two oxygen atoms. However, the total energy of the  $CO_2$  molecule, which is subtracted from the sum of the energies of the oxygen atom and carbon monoxide molecule to determine the  $O-CO$  bond energy, is increased by

the ionization energies of  $C$ ,  $C^+$ ,  $O$ , and  $2O^+$  given by Eqs. (14.12-14.15), respectively. Experimentally, the energies are [2]

$$E(\text{ionization}; C) = 11.26030 \text{ eV} \quad (14.12)$$

$$E(\text{ionization}; C^+) = 24.38332 \text{ eV} \quad (14.13)$$

$$5 \quad E(\text{ionization}; O) = 13.61806 \text{ eV} \quad (14.14)$$

$$E(\text{ionization}; O^+) = 35.11730 \text{ eV} \quad (14.15)$$

In addition, the central forces on the  $2p$  shell of the  $O$  atom are increased with the formation of the  $\sigma$  MO which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of each  $O$  atom at the new radius are calculated  
10 and added to the ionization energies of  $C$ ,  $C^+$ ,  $O$ , and  $2O^+$ , and the energy of the  $\sigma$  MO to give the total energy of  $CO_2$ . Then, the bond energy is determined from the total  $CO_2$  energy.

The radius  $r_8$  of each oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 \quad (14.16)$$

15 Using the initial radius  $r_8$  of each  $O$  atom and the final radius  $r_6$  of the  $O2p$  shell (Eq. (14.11)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(O, 2p)$  of the Coulombic energy change of the  $O2p$  electrons of each  $O$  atom is determined using Eq. (10.102):

$$\begin{aligned} E_T(O, 2p) &= -\sum_{n=4}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_8} \right) \\ &= -(13.60580 \text{ eV})(0.33733)(3+4) \\ &= -32.12759 \text{ eV} \end{aligned} \quad (14.17)$$

20

## FORCE BALANCE OF THE $\sigma$ MO OF THE CARBON DIOXIDE MOLECULE

As in the case of  $H_2$ , the  $\sigma$  MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the  $C$  atom for distances shorter than the radius of the  $C2s$   
25 shell; nor, can it extend into the  $O$  atom for distances shorter than the radius of the  $O2p$  shell. Thus, the MO surface of each  $C=O$  bond comprises a prolate spheroid that bridges and is continuous with the  $2s$  and  $2p$  shells of the  $O$  and  $C$  atoms whose nuclei serve as the foci. The energy of each prolate spheroid is matched to that of the  $C2s$  and  $O2p$  shells.

As in the case of previous examples of energy-matched MOs such as  $OH$  and  $NH$ , the  $C=O$ -bond MO must comprise 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. However, the paired electrons of the  $C2s$  and  $O2p$  shells are not involved in bonding. Rather, the AOs permit a continuous surface

5 comprising the two  $C=O$ -bond MOs having six paired electrons, two from each of the  $C$  and the two  $O$  atoms:



10 The force balance of the  $CO_2$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.18) and the energy matching condition between the carbon and oxygen components of the MO.

Similar to the  $OH$  and  $H_2O$  cases given by Eqs. (13.57) and (13.162), the  $H_2$ -type ellipsoidal MO comprises 75% of the  $CO_2$  MO; so, the electron charge density in Eq. (11.65)

15 is given by  $-0.75e$ . Thus,  $k'$  of the each  $H_2$ -type-ellipsoidal-MO component of the  $CO_2$  MO is given by Eq. (13.59). The distance from the origin of each  $C=O$ -bond MO to each focus  $c'$  is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal  $C=O$ -bond MO  $b=c$  given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). Then, the solution of the semimajor

20 axis  $a$  allows for the solution of the other axes of the prolate spheroidal and eccentricity of the  $CO_2$  MO.

The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  of the  $CO_2$   $\sigma$  MO are the same as those of  $OH$  given by Eqs. (13.67-13.73), except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to each  $\sigma$ -MO double

25 bond:

$$E_T(C=O, \sigma) = -\frac{4e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \quad (14.19)$$

where  $E_T(C=O, \sigma)$  is the total energy of each  $C=O$   $\sigma$  MO of  $CO_2$ . The total energy of a  $H_2$ -type ellipsoidal MO is given by Eqs. (11.212) and (13.75). A minimum energy is obtained when each double bond of the  $\sigma$  MO of  $CO_2$  comprises the energy equivalent of

30 four  $H_2$ -type ellipsoidal MOs. For each  $C=O$  bond to match the energy of the  $C2s$  orbital,

the ionization energy of  $C$  and  $C^+$  (Eqs. (14.12-14.13)) must be added for each bond of the double bond. Thus, the total energy of each  $C=O$ -bond MOs is

$$\begin{aligned}
 E_T(C=O, \sigma) &= 2 \left( 2 \left( -\frac{e^2}{8\pi\epsilon_0 a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] \right) \right. \\
 &\quad \left. + E(\text{ionization}; C) + E(\text{ionization}; C^+) \right) \\
 &= 2 \left( 2(-31.63536831 \text{ eV}) + 11.26030 \text{ eV} + 24.38332 \text{ eV} \right) \\
 &= -55.25423 \text{ eV}
 \end{aligned} \tag{14.20}$$

$E_T(C=O, \sigma)$  given by Eq. (14.19) is set equal to Eq. (14.20):

$$5 \quad \frac{4e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} \right) \ln \frac{a+c'}{a-c'} - 1 \right] = e55.25423 \text{ eV} \tag{14.21}$$

From the energy relationship given by Eq. (14.21) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CO_2$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.21) gives

$$E_T(C=O, \sigma) = \frac{4e^2}{8\pi\epsilon_0 \sqrt{\frac{2aa_0}{3}}} \left[ \left( \frac{3}{2} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right] = e55.25423 \text{ eV} \tag{14.22}$$

10 The most convenient way to solve Eq. (14.22) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.80703a_0 = 9.56239 \times 10^{-11} \text{ m} \tag{14.23}$$

Substitution of Eq. (14.23) into Eq. (13.60) is

$$c' = 1.09758a_0 = 5.80815 \times 10^{-11} \text{ m} \tag{14.24}$$

15 The internuclear distance given by multiplying Eq. (14.24) by two is

$$2c' = 2.19516a_0 = 1.16163 \times 10^{-10} \text{ m} \tag{14.25}$$

The experimental bond distance is [3]

$$2c' = 1.1600 \times 10^{-10} \text{ m} \tag{14.26}$$

Substitution of Eqs. (14.23-14.24) into Eq. (13.62) is

$$20 \quad b = c = 1.43550a_0 = 7.59636 \times 10^{-11} \text{ m} \tag{14.27}$$

Substitution of Eqs. (14.23-14.24) into Eq. (13.63) is

$$e = 0.60740 \tag{14.28}$$

The  $C$  and  $O$  nuclei comprise the foci of each  $H_2$ -type ellipsoidal MO defined as  $O=C=O$ . Consider the left-hand  $C=O$  bond of the two equivalent bonds in the absence



of the right-hand bond. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C2s$  AO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_4 = 0.84317a_0$  is the radius of the  $C2s$  shell. Substitution of Eqs. (14.23-14.24) into Eq. (13.261) gives

$$5 \quad \theta' = 54.53^\circ \quad (14.29)$$

Then, the angle  $\theta_{C2sAO}$  the radial vector of the  $C2s$  AO makes with the internuclear axis is

$$\theta_{C2sAO} = 180^\circ - 54.53^\circ = 125.47^\circ \quad (14.30)$$

as shown in Figure 33. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{H_2MO}$

10 between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C2s$  radial vector obeys the following relationship:

$$r_4 \sin \theta_{C2sAO} = 0.84317a_0 \sin \theta_{C2sAO} = b \sin \theta_{H_2MO} \quad (14.31)$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{0.84317a_0 \sin \theta_{C2sAO}}{b} = \sin^{-1} \frac{0.84317a_0 \sin 125.47^\circ}{b} \quad (14.32)$$

15 with the use of Eq. (14.30). Substitution of Eq. (14.27) into Eq. (14.32) gives

$$\theta_{H_2MO} = 28.58^\circ \quad (14.33)$$

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a \cos \theta_{H_2MO} \quad (14.34)$$

20 Substitution of Eqs. (14.23) and (14.33) into Eq. (14.34) gives

$$d_{H_2MO} = 1.58687a_0 = 8.39737 \times 10^{-11} \text{ m} \quad (14.35)$$

The distance  $d_{C2sAO}$  along the internuclear axis from the origin of the  $C$  atom to the point of intersection of the orbitals is given by

$$d_{C2sAO} = d_{H_2MO} - c' \quad (14.36)$$

25 Substitution of Eqs. (14.24) and (14.35) into Eq. (14.36) gives

$$d_{C2sAO} = 0.48929a_0 = 2.58922 \times 10^{-11} \text{ m} \quad (14.37)$$

The  $C$  and  $O$  nuclei comprise the foci of each  $H_2$ -type ellipsoidal MO defined as  $O=C=O$ . Consider the right-hand  $C=O$  bond of the two equivalent bonds. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $O2p$  AO are

given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_6 = 0.74776a_0$  is the radius of the  $O2p$  shell. Substitution of Eqs. (14.23-14.24) into Eq. (13.261) gives

$$\theta' = 30.18^\circ \quad (14.38)$$

5 Then, the angle  $\theta_{O2pAO}$  the radial vector of the  $O2p$  AO makes with the internuclear axis is

$$\theta_{O2pAO} = 180^\circ - 30.18^\circ = 149.82^\circ \quad (14.39)$$

as shown in Figure 33. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO

10 with the  $O2p$  radial vector obeys the following relationship:

$$r_6 \sin \theta_{O2pAO} = 0.74776a_0 \sin \theta_{O2pAO} = b \sin \theta_{H_2MO} \quad (14.40)$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{0.74776a_0 \sin \theta_{O2pAO}}{b} = \sin^{-1} \frac{0.74776a_0 \sin 149.82^\circ}{b} \quad (14.41)$$

with the use of Eq. (14.39). Substitution of Eq. (14.27) into Eq. (14.41) gives

$$15 \quad \theta_{H_2MO} = 15.18^\circ \quad (14.42)$$

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a \cos \theta_{H_2MO} \quad (14.43)$$

Substitution of Eqs. (14.23) and (14.42) into Eq. (14.43) gives

$$20 \quad d_{H_2MO} = 1.74396a_0 = 9.22862 \times 10^{-11} \text{ m} \quad (14.44)$$

The distance  $d_{O2pAO}$  along the internuclear axis from the origin of each  $O$  atom to the point of intersection of the orbitals is given by

$$d_{2pAO} = d_{H_2MO} - c' \quad (14.45)$$

Substitution of Eqs. (14.24) and (14.44) into Eq. (14.45) gives

$$25 \quad d_{O2pAO} = 0.64637a_0 = 3.42047 \times 10^{-11} \text{ m} \quad (14.46)$$

As shown in Eq. (14.18), each  $C=O$  bond comprises a factor of 0.75 of the charge-density of double that of the  $H_2$ -type ellipsoidal MO. Using the electron configuration of  $CO_2$  (Eq. (14.2)), the radii of the  $C1s = 0.17113a_0$  (Eq. (10.51)),  $C2s = 0.84317a_0$  (Eq. (10.62)),  $O1s = 0.12739a_0$  (Eq. (10.51)),  $O2s = 0.59020a_0$  (Eq. (10.62)), and

$O2p = 0.74776a_0$  (Eq. (14.11)) shells and the parameters of the  $\sigma$  MO of  $CO_2$  given by Eqs. (13.3-13.4), (14.23-14.25), and (14.27-14.28), the dimensional diagram and charge-density of the  $CO_2$  MO are shown in Figures 33 and 34, respectively.

## 5 SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE CARBON DIOXIDE MOLECULE

The energies of the  $CO_2$   $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. (14.23-14.24) and (14.27)) into the energy equations of  $OH$  (Eqs. (13.67-13.73)), except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by

10 two due to each  $\sigma$ -MO double bond:

$$V_e = 2^2 \left( \frac{3}{4} \right) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -104.83940 \text{ eV} \quad (14.47)$$

$$V_p = 2^2 \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 49.58464 \text{ eV} \quad (14.48)$$

$$T = 2 \left( \frac{3}{4} \right) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 14.50438 \text{ eV} \quad (14.49)$$

$$V_m = 2^2 \left( \frac{3}{4} \right) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -14.50438 \text{ eV} \quad (14.50)$$

$$15 \quad E_T = V_e + T + V_m + V_p \quad (14.51)$$

Substitution of Eqs. (13.60) and (14.47-14.50) into Eq. (14.51) gives

$$E_T(C=O, \sigma) = V_e + T + V_m + V_p = \frac{-4e^2}{8\pi\epsilon_0\sqrt{\frac{2aa_0}{3}}} \left[ \left( \frac{3}{2} \right) \ln \frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}} - 1 \right] = -55.25476 \text{ eV} \quad (14.52)$$

where  $E_T(C=O, \sigma)$  is the total energy of each  $C=O$   $\sigma$  MO of  $CO_2$  given by Eq. (14.19)

20 which is reiteratively matched to Eq. (14.20) within five-significant-figure round off error.

The total energy of  $CO_2$ ,  $E_T(CO_2)$ , is given by the sum of  $E(\text{ionization}; C)$  and  $E(\text{ionization}; C^+)$ , the sum of the energies of the first and second electrons of carbon (Eqs. (14.12-14.13)) donated to each double bond, the sum of  $E(\text{ionization}; O)$  and two times  $E(\text{ionization}; O^+)$ , the energies of the first and second electrons of oxygen (Eqs. (14.14-

14.15)) donated to the double bonds, two times  $E_T(O, 2p)$ , the  $O2p$  AO contribution due to the decrease in radius with the formation of each bond (Eq. (14.17)), and two times  $E_T(C=O, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (14.22):

$$\begin{aligned}
 E_T(CO_2) &= \left( E(\text{ionization}; C) + E(\text{ionization}; C^+) + E(\text{ionization}; O) \right. \\
 &\quad \left. + 2E(\text{ionization}; O^+) + 2E_T(O, 2p) + 2E_T(C=O, \sigma) \right) \\
 &= \left( 11.26030 \text{ eV} + 24.38332 \text{ eV} + 13.61806 \text{ eV} \right. \\
 &\quad \left. + 2(35.11730 \text{ eV}) + 2(-32.12759 \text{ eV}) \right. \\
 &\quad \left. - 2 \left( \frac{4e^2}{8\pi\epsilon_0 \sqrt{\frac{2aa_0}{3}}} \left( \left( \frac{3}{2} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right) \right) \right) \\
 &= \left( 11.26030 \text{ eV} + 24.38332 \text{ eV} + 13.61806 \text{ eV} \right. \\
 &\quad \left. + 2(35.11730 \text{ eV}) + 2(-32.12759 \text{ eV}) - 2(55.25423 \text{ eV}) \right) \\
 &= -55.26841 \text{ eV}
 \end{aligned} \tag{14.53}$$

5

## VIBRATION OF $CO_2$

The vibrational energy levels of  $CO_2$  may be solved by determining the Morse potential curve from the energy relationships for the transition from a  $C$  atom and two  $O$  atoms whose parameters are given by Eqs. (10.115-10.123) and (10.154-10.163), respectively, to a  $C$  atom whose parameter  $r_4$  is given by Eq. (10.61), two  $O$  atoms whose parameter  $r_6$  is given by Eq. (14.11), and the  $\sigma$   $CO_2$  MO whose parameters are given by Eqs. (14.23-14.25) and (14.27-14.28). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [4] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF THE CARBON DIOXIDE MOLECULE

The equations of the radiation reaction force of carbon dioxide are the same as those of  $OH$  with the substitution of the  $CO_2$  parameters except that there is a factor of four increase in the

central force in Eq. (13.140) due to the double bond. Using Eqs. (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{4(0.75)e^2}{4\pi\epsilon_0 b^3}} = 4.16331 \times 10^{16} \text{ rad/s} \quad (14.54)$$

where  $b$  is given by Eq. (14.27). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. 5 (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 4.16331 \times 10^{16} \text{ rad/s} = 27.40365 \text{ eV} \quad (14.55)$$

In Eq. (11.181), substitution of  $E_T(CO_2)/2$  for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (14.55) for  $\bar{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

$$10 \quad \bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -27.63421 \text{ eV} \sqrt{\frac{2e(27.40365 \text{ eV})}{m_e c^2}} = -0.28619 \text{ eV} \quad (14.56)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The transition state comprises  $O--CO$ , oxygen binding to  $CO$ . Vibration of the linear XYZ-molecular transition state corresponds to  $\nu_3$  [5] with the maximum kinetic energy localized to the nascent  $C-O$  bond. In this case, 15 the kinetic energy of the nuclei is the maximum for this bond. Thus,  $\bar{E}_{Kvib}$  is the vibrational energy. The decrease in the energy of the  $CO_2$  MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (14.56) and  $\bar{E}_{Kvib}$ , the vibrational energy. Using the experimental  $CO_2$   $E_{vib}(\nu_3)$  of  $2349 \text{ cm}^{-1}$  ( $0.29124 \text{ eV}$ ) [6] for  $\bar{E}_{Kvib}$  of 20 the transition state,  $\bar{E}_{osc}(CO_2)$  is

$$\bar{E}_{osc}(CO_2) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + E_{vib} \quad (14.57)$$

$$\bar{E}_{osc}(CO_2) = -0.28619 \text{ eV} + 0.29124 \text{ eV} = 0.00505 \text{ eV} \quad (14.58)$$

## TOTAL AND BOND ENERGIES OF THE CARBON DIOXIDE MOLECULE

$E_{T+osc}(CO_2)$ , the total energy of  $CO_2$  including the Doppler term, is given by the sum of  $E_T(CO_2)$  (Eq. (14.53)) and  $\bar{E}_{osc}(CO_2)$  given by Eq. (14.58):

$$\begin{aligned}
 E_{T+osc}(CO_2) &= \left( \begin{aligned} &2(V_e + T + V_m + V_p) + E(\text{ionization}; C) \\ &+ E(\text{ionization}; C^+) + E(\text{ionization}; O) + 2E(\text{ionization}; O^+) \\ &+ 2E_T(O, 2p) + \bar{E}_{osc}(CO_2) \end{aligned} \right) \\
 &= \left( \begin{aligned} &2E_T(C=O, \sigma) + E(\text{ionization}; C) + E(\text{ionization}; C^+) \\ &+ E(\text{ionization}; O) + 2E(\text{ionization}; O^+) \\ &+ 2E_T(O, 2p) + \bar{E}_{osc}(CO_2) \end{aligned} \right) \quad (14.59) \\
 &= E_T(CO_2) + \bar{E}_{osc}(CO_2)
 \end{aligned}$$

$$\begin{aligned}
 E_{T+osc}(CO_2) &= \left( \begin{aligned} &2 \left( \frac{-4e^2}{8\pi\epsilon_0 \sqrt{\frac{2aa_0}{3}}} \left( \left( \frac{3}{2} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right) \right) + E(\text{ionization}; C) \\ &+ E(\text{ionization}; C^+) + E(\text{ionization}; O) \\ &+ 2E(\text{ionization}; O^+) - 2 \sum_{O, n=4}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_8} \right) \\ &\left( 1 + \frac{1}{2} \sqrt{\frac{2\hbar \sqrt{\frac{4(0.75)e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2}} \right) + E_{vib} \end{aligned} \right) \\
 &= -55.26841 \text{ eV} - 0.28619 \text{ eV} + E_{vib} \quad (14.60)
 \end{aligned}$$

From Eqs. (14.57-14.60), the total energy of the  $CO_2$  MO is

$$\begin{aligned}
 E_{T+osc}(CO_2) &= -55.25476 \text{ eV} + \bar{E}_{osc}(CO_2) \\
 &= -55.25476 \text{ eV} + 0.00505 \text{ eV} \\
 &= -55.26336 \text{ eV} \quad (14.61)
 \end{aligned}$$

where the experimental  $E_{vib}$  was used.

As in the case of the dissociation of the bond of the hydroxyl radical, an oxygen atom is formed with dissociation of  $CO_2$ .  $O$  has two unpaired electrons as shown in Eq. (13.55) which interact to stabilize the atom as shown by Eq. (10.161-10.162). The lowering of the energy of the reactants decreases the bond energy. Thus, the total energy of oxygen is

reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.101):

$$E(\text{magnetic}) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 a_0^3} = \frac{8\pi\mu_0 \mu_B^2}{a_0^3} = 0.11441 \text{ eV} \quad (14.62)$$

The  $CO_2$  bond dissociation energy,  $E_D(CO_2)$ , is given by the sum of the energies of the  $CO$  and the  $O$  atom minus the sum of  $E_{T+osc}(CO_2)$  and  $E(\text{magnetic})$ :

$$E_D(CO_2) = E(CO) + E(O) - (E(\text{magnetic}) + E_{T+osc}(CO_2)) \quad (14.63)$$

The energy of an oxygen atom is given by Eq. (14.14) and  $E_T(CO)$  is given by the sum of the experimental energies of  $C$  (Eq. (14.12)),  $O$  (Eq. (14.14)), and the negative of the bond energy of  $CO$  (Eq. (13.914)):

$$E(CO) = -11.26030 \text{ eV} - 13.618060 \text{ eV} - 11.15696 \text{ eV} = -36.03532 \text{ eV} \quad (14.64)$$

The energy of  $O$  is given by the negative of the corresponding ionization energy given in Eq. (4.14). Thus, the  $CO_2$  bond dissociation energy,  $E_D(CO_2)$ , given by the Eqs. (4.14) and (14.61-14.64) is

$$\begin{aligned} E_D(CO_2) &= -(36.03532 \text{ eV} + 13.618060 \text{ eV}) - (E(\text{magnetic}) + E_{T+osc}(CO_2)) \\ &= -49.65338 \text{ eV} - (0.11441 \text{ eV} - 55.26336 \text{ eV}) \\ &= 5.49557 \text{ eV} \end{aligned} \quad (14.65)$$

The experimental  $CO_2$  bond dissociation energy is [7]

$$E_{D298}(CO_2) = 5.516 \text{ eV} \quad (14.66)$$

The results of the determination of bond parameters of  $CO_2$  are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## NITROGEN DIOXIDE MOLECULE

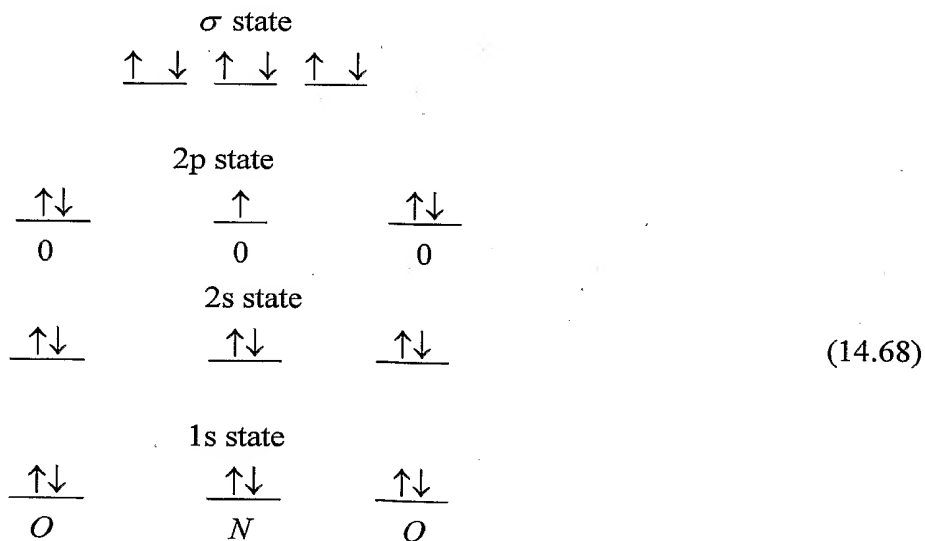
The nitrogen dioxide molecule can be formed by the reaction of nitric oxide and an oxygen atom:



The bonding in the nitrogen dioxide molecule comprises two double bonds, each a  $H_2$ -type MO with four paired electrons wherein the central  $N$  atom is shared by both bonds such that six electrons can be assigned to the two  $N=O$  bonds. Thus, two  $N2p$  electrons combine

with the four  $O2p$  electrons, two from each  $O$ , as a linear combination to form the two overlapping  $N=O$  bonds of  $NO_2$ . The force balance equation and radius  $r_7$  of the  $2p$  shell of  $N$  is derived in the Seven-Electron Atoms section. The force balance equation and radius  $r_8$  of the  $2p$  shell of  $O$  is derived in the Eight-Electron Atoms section. With the formation of each of the two  $H_2$ -type MOs by the contribution of two  $2p$  electrons each from the  $N$  and  $O$  atoms, a diamagnetic force arises between the remaining outer shell atomic electrons, the  $2s$  and  $2p$  electrons of  $N$  and  $O$ , and the  $H_2$ -type MO. This force from  $N$  and  $O$  causes the  $H_2$ -type MO to move to greater principal axes than would result with the Coulombic force alone. But, the factor of two increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining  $N$  and  $O$  electrons decrease the radii of the corresponding shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of  $NO_2$  is  $N1s^2O_11s^2O_21s^2N2s^2O_12s^2O_22s^2N2p^1O_12p^2O_22p^2\sigma_{O_2,N,O_1}^6$  where the subscripts designate the  $O$  atom, 1 or 2,  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is

15



Nitrogen dioxide is predicted to be weakly paramagnetic in agreement with observations [1].



# FORCE BALANCE OF THE $2p$ SHELL OF THE NITROGEN ATOM OF NITROGEN DIOXIDE

For the  $N$  atom, force balance for the outermost  $2p$  electron of  $NO_2$  (electron 5) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to 5 interactions between electron 5 and the  $2s$ -shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central Coulomb force on the outer-most  $2p$  shell electron of  $NO$  (electron 5) due to the nucleus and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\epsilon_0 r_5^2} \mathbf{i}_r \quad (14.69)$$

10 for  $r > r_4$ . The  $2p$  shell possess a +2 external electric field given by Eq. (10.92) for  $r > r_5$ . The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces of  $N$  in  $NO_2$  are the same as those of  $N$  in  $NO$ . They are also the same as those of  $N$  in the nitrogen molecule with  $r_5$  replacing  $r_6$  and with an increase of the central field by an integer. The diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the  $p$ -  
15 orbital contribution is given by Eq. (13.918):

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right) \frac{\hbar^2}{4m_e r_5^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{\hbar^2}{12m_e r_5^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r \quad (14.70)$$

And,  $\mathbf{F}_{mag\ 2}$  corresponding to the conserved orbital angular momentum of the three orbitals is also the same as that of  $NO_2$  given by Eq. (13.919):

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{3\hbar^2}{m_e r_5^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (14.71)$$

20 The electric field external to the  $2p$  shell given by Eq. (10.92) for  $r > r_5$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the  $p$ -orbital electron having an electric field of +2 outside of its radius is given by Eq. (13.920):

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_5^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (14.72)$$

25 The radius of the  $2p$  shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (14.69)) and diamagnetic (Eqs. (14.70) and (14.72)), and paramagnetic (Eq. (14.71)) forces as follows:

$$\frac{m_e v_s^2}{r_s} = \left( \frac{(Z-4)e^2}{4\pi\epsilon_0 r_s^2} - \frac{\hbar^2}{12m_e r_s^2 r_3} \sqrt{s(s+1)} + \frac{3\hbar^2}{Zm_e r_s^2 r_3} \sqrt{s(s+1)} \right) - \left[ \frac{Z-5}{Z-4} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_s^4 m_e} 10 \sqrt{s(s+1)} \quad (14.73)$$

Substitution of  $v_s = \frac{\hbar}{m_e r_s}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (14.73) gives:

$$\frac{\hbar^2}{m_e r_s^3} = \frac{(Z-4)e^2}{4\pi\epsilon_0 r_s^2} - \frac{\hbar^2}{12m_e r_s^2 r_3} \sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Zm_e r_s^2 r_3} \sqrt{\frac{3}{4}} - \left[ \frac{Z-5}{Z-4} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_s^4 m_e} 10 \sqrt{\frac{3}{4}} \quad (14.74)$$

The quadratic equation corresponding to Eq. (14.74) is

$$5 \quad r_s^2 - \frac{\frac{\hbar^2}{m_e}}{\left( \frac{(Z-4)e^2}{4\pi\epsilon_0} - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} r_s - \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-5}{Z-4} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-4)e^2}{4\pi\epsilon_0} - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} = 0 \quad (14.75)$$

The solution of Eq. (14.75) using the quadratic formula is:

$$r_s = \frac{\left( (Z-4) - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\sqrt{3}}{2r_3} \right) \pm a_0}{2} \sqrt{\frac{1}{\left( (Z-4) - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)^2} + \frac{20\sqrt{3} \left[ \frac{Z-5}{Z-4} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3}{\left( (Z-4) - \left( \frac{1}{12} - \frac{3}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)}} \quad (14.76)$$

$r_3$  in units of  $a_0$

The positive root of Eq. (14.76) must be taken in order that  $r_s > 0$ . Substitution of

10  $\frac{r_3}{a_0} = 0.69385$  (Eq. (10.62) with  $Z = 7$ ) into Eq. (14.76) gives

$$r_s = 0.74841 a_0 \quad (14.77)$$

## FORCE BALANCE OF THE $2p$ SHELL OF EACH OXYGEN ATOM OF NITROGEN DIOXIDE

15 For each  $O$  atom, force balance for the outermost  $2p$  electron of  $NO_2$  (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due

to interactions between electron 6 and the other  $2p$  electron as well as the  $2s$ -shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most  $2p$  shell electron of  $NO_2$  (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the  
 5 appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} \mathbf{i}_r \quad (14.78)$$

for  $r > r_5$ . The  $2p$  shell possess an external electric field of +2 given by Eq. (10.92) for  $r > r_6$ . The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces of  $O$  in  $NO_2$  are the same as those of  $O$  in  $NO$ . The  
 10 diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the  $p$ -orbital contribution given by Eq. (13.927) is

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right) \frac{\hbar^2}{4m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r \quad (14.79)$$

And,  $\mathbf{F}_{mag\ 2}$  corresponding to the conserved spin and orbital angular momentum given by Eq. (13.928) is

$$15 \quad \mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{2\hbar^2}{m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \quad (14.80)$$

The electric field external to the  $2p$  shell given by Eq. (10.92) for  $r > r_6$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the  $p$ -orbital electron having an electric field of +2 outside of its radius given by Eq. (13.929) is

$$20 \quad \mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10 \sqrt{s(s+1)} \mathbf{i}_r \quad (14.81)$$

In addition, the contribution of two  $2p$  electrons in the formation of the  $\sigma$  MO gives rise to a paramagnetic force on the remaining paired  $2p$  electrons. The force  $\mathbf{F}_{mag\ 3}$  is given by Eq. (13.930) is

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \mathbf{i}_r \quad (14.82)$$

25 The radius of the  $2p$  shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (14.78)) and diamagnetic (Eqs. (14.79) and (14.81)), and

paramagnetic (Eqs. (14.80) and (14.82)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \left( \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{s(s+1)} \right) - \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \right) \quad (14.83)$$

Substitution of  $v_6 = \frac{\hbar}{m_e r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (14.83) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3} \sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\epsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{\frac{3}{4}} - \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{\frac{3}{4}} \quad (14.84)$$

5

The quadratic equation corresponding to Eq. (14.84) is

$$r_6^2 - \frac{\frac{\hbar^2}{m_e} \left( 1 - \frac{\sqrt{3}}{8} \right)}{\left( \frac{(Z-5)e^2}{4\pi\epsilon_0} - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} r_6 - \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z-5)e^2}{4\pi\epsilon_0} - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} = 0 \quad (14.85)$$

The solution of Eq. (14.85) using the quadratic formula is:

$$r_6 = \frac{a_0 \left( 1 - \frac{\sqrt{3}}{8} \right)}{\left( (Z-5) - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)} \pm a_0 \sqrt{\frac{\left( \frac{1 - \frac{\sqrt{3}}{8}}{\left( (Z-5) - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)} \right)^2 + \frac{20\sqrt{3} \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3}{\left( (Z-5) - \left( \frac{2}{12} - \frac{2}{Z} \right) \frac{\sqrt{3}}{2r_3} \right)}}}{2} \quad (14.86)$$

$r_3$  in units of  $a_0$

The positive root of Eq. (14.86) must be taken in order that  $r_6 > 0$ . Substitution of

$\frac{r_3}{a_0} = 0.59020$  (Eq. (10.62) with  $Z = 8$ ) into Eq. (14.86) gives

$$r_6 = 0.70460 a_0 \quad (14.87)$$

## OXYGEN ATOMS OF NITROGEN DIOXIDE

Consider the determination of the total energy of  $NO_2$  from the reaction of a nitrogen atom with two oxygen atoms. With the formation of each  $H_2$ -type MO by the contribution of two  $2p$  electrons from each of the  $N$  and the two  $O$  atoms, the total energy of the  $NO_2$  molecule, which is subtracted from the sum of the energies of the nitrogen and oxygen atoms to determine the bond energy, is increased by the ionization energies of  $N$ ,  $N^+$ ,  $O$ , and  $2O^+$  given by Eqs. (14.88-14.91), respectively. Experimentally, the energies are [2]

$$E(\text{ionization}; N) = 14.53414 \text{ eV} \quad (14.88)$$

$$E(\text{ionization}; N^+) = 29.6013 \text{ eV} \quad (14.89)$$

$$10 \quad E(\text{ionization}; O) = 13.61806 \text{ eV} \quad (14.90)$$

$$E(\text{ionization}; O^+) = 35.11730 \text{ eV} \quad (14.91)$$

In addition, the central forces on the  $2p$  shells of the  $N$  and  $O$  atoms are increased with the formation of the  $\sigma$  MOs which reduces each shell's radius and increases its total energy. The change per bond is the same as that of  $NO$  since the final radii given by Eq. (14.77) and (14.87) are the same for  $NO$  and  $NO_2$ . The Coulombic energy terms of the total energy of the  $N$  and  $O$  atoms at the new radii are calculated and added to the ionization energies of  $N$ ,  $N^+$ ,  $O$ , and  $2O^+$ , and the energy of the  $\sigma$  MOs to give the total energy of  $NO_2$ . Then, the bond energy is determined from the total  $NO_2$  energy.

The radius  $r_7$  of the nitrogen atom before bonding is given by Eq. (10.142):

$$20 \quad r_7 = 0.93084a_0 \quad (14.92)$$

Using the initial radius  $r_7$  of the  $N$  atom and the final radius  $r_5$  of the  $N2p$  shell (Eq. (14.77)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(N, 2p)$  of the Coulombic energy change of the  $N2p$  electrons of the  $N$  atom is determined using Eq. (10.102):

$$\begin{aligned} E_T(N, 2p) &= -\sum_{n=4}^4 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_5} - \frac{1}{r_7} \right) \\ 25 \quad &= -(13.60580 \text{ eV})(0.26186)(3) \\ &= -10.68853 \text{ eV} \end{aligned} \quad (14.93)$$

The radius  $r_8$  of the oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 \quad (14.94)$$

Using the initial radius  $r_8$  of the  $O$  atom and the final radius  $r_6$  of the  $O2p$  shell (Eq. (14.87)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(O, 2p)$  of the Coulombic energy change of the  $O2p$  electrons of the  $O$  atom is determined using Eq. (10.102):

$$\begin{aligned}
 E_T(O, 2p) &= \sum_{n=4}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_8} \right) \\
 &= (13.60580 \text{ eV}) (0.41925a_0^{-1}) (3+4) \\
 &= -39.92918 \text{ eV}
 \end{aligned}
 \tag{14.95}$$

### FORCE BALANCE OF THE $\sigma$ MO OF NITROGEN DIOXIDE

The force balance can be considered due to a second pair of two electrons binding to a molecular ion having  $+2e$  at each focus and a first bound pair. Then, the forces are the same as those of a molecule ion having  $+e$  at each focus. The diamagnetic force  $\mathbf{F}_{\text{diamagneticMO1}}$  for each  $\sigma$ -MO of the  $NO_2$  molecule due to the two paired electrons in the  $O2p$  shell is given by Eq. (13.633) with  $n_e = 2$ :

$$\mathbf{F}_{\text{diamagneticMO1}} = \frac{\hbar^2}{2m_e a^2 b^2} D \mathbf{i}_\xi \tag{14.96}$$

This is also the corresponding force of  $NO$  given by Eq. (13.942).  $\mathbf{F}_{\text{diamagneticMO2}}$  of the nitrogen dioxide molecule comprising nitrogen with charge  $Z_1 = 7$  and  $|L_1| = \hbar$  and  $|L_2| = \sqrt{\frac{3}{4}}\hbar$  and the two oxygen atoms, each with  $Z_2 = 8$  and  $|L_3| = \hbar$  is given by the corresponding sum of the contributions. Using Eq. (13.835),  $\mathbf{F}_{\text{diamagneticMO2}}$  for  $NO_2$  is

$$\mathbf{F}_{\text{diamagneticMO2}} = \left( \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D \mathbf{i}_\xi \tag{14.97}$$

This is also the corresponding force of  $NO$  given by Eq. (13.943) except the term due to oxygen is twice that of  $NO$  due to the two oxygen atoms of  $NO_2$ . The general force balance equation for the  $\sigma$ -MO of the nitrogen dioxide molecule given by Eqs. (11.200), and (14.97-14.98) is also the same as that of  $CN$  (Eq. (14.836)) except for the doubling of the  $\frac{2}{Z_2}$  term due to the two oxygen atoms:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left( 1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D \quad (14.98)$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 ab^2} D - \left( \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D \quad (14.99)$$

$$\left( 2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 ab^2} D \quad (14.100)$$

$$a = \left( 2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2} \right) a_0 \quad (14.101)$$

5 Substitution of  $Z_1 = 7$  and  $Z_2 = 8$  into Eq. (14.101) gives

$$a = 2.51658a_0 = 1.33171 \times 10^{-10} \text{ m} \quad (14.102)$$

Substitution of Eq. (14.102) into Eq. (11.79) is

$$c' = 1.12173a_0 = 5.93596 \times 10^{-11} \text{ m} \quad (14.103)$$

The internuclear distance given by multiplying Eq. (14.103) by two is

$$10 \quad 2c' = 2.24347a_0 = 1.18719 \times 10^{-10} \text{ m} \quad (14.104)$$

The experimental bond distance is [3]

$$2c' = 1.193 \times 10^{-10} \text{ m} \quad (14.105)$$

Substitution of Eqs. (14.102-14.103) into Eq. (11.80) is

$$b = c = 2.25275a_0 = 1.19210 \times 10^{-10} \text{ m} \quad (14.106)$$

15 Substitution of Eqs. (14.102-14.103) into Eq. (11.67) is

$$e = 0.44574 \quad (14.107)$$

The bonding in the nitrogen dioxide molecule comprises two double bonds, each a  $H_2$ -type MO with four paired electrons wherein the central  $N$  atom is shared by both bonds such that six electrons can be assigned to the two  $N=O$  bonds. Thus, two  $N2p$  electrons combine with the four  $O2p$  electrons, two from each  $O$ , as a linear combination to form the two overlapping  $N=O$  bonds of  $NO_2$ . Using the electron configuration of  $NO_2$  (Eq.

20

(14.68)), the radii of the  $N1s = 0.14605a_0$  (Eq. (10.51)),  $N2s = 0.69385a_0$  (Eq. (10.62)),  $N2p = 0.74841a_0$  (Eq. (14.77)),  $O1s = 0.12739a_0$  (Eq. (10.51)),  $O2s = 0.59020a_0$  (Eq. (10.62)), and  $O2p = 0.70460a_0$  (Eq. (14.87)) shells and the parameters of the  $\sigma$  MOs of  $NO_2$  given by Eqs. (13.3-13.4), (14.102-14.104), and (14.106-14.107), the dimensional  
5 diagram and charge-density of the  $NO_2$  MO are shown in Figures 35 and 36, respectively.

## SUM OF THE ENERGIES OF THE $\sigma$ MOs AND THE AOs OF NITROGEN DIOXIDE

The energies of each  $NO_2$   $\sigma$  MO are the same as those of  $NO$  (Eqs. (13.954-13.958)). They  
10 are given by the substitution of the semiprincipal axes (Eqs. (14.102-14.103) and (14.106)) into the energy equations (Eqs. (11.207-11.212)) of  $H_2$  except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the  $\sigma$ -MO double bond with two pairs of paired electrons:

$$V_e = 2^2 \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -93.03032 \text{ eV} \quad (14.108)$$

$$15 \quad V_p = 2^2 \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 48.51704 \text{ eV} \quad (14.109)$$

$$T = 2 \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 9.24176 \text{ eV} \quad (14.110)$$

$$V_m = 2^2 \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -9.24176 \text{ eV} \quad (14.111)$$

$$E_T = V_e + T + V_m + V_p \quad (14.112)$$

Substitution of Eqs. (11.79) and (14.108-14.111) into Eq. (14.112) gives

$$20 \quad E_T(N=O, \sigma) = \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left( 8 \ln \frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}} - 4 \right) = -44.51329 \text{ eV} \quad (14.113)$$

where  $E_T(N=O, \sigma)$  is the total energy of each  $\sigma$  MO of  $NO_2$ . The total energy of  $NO_2$ ,  $E_T(NO_2)$ , is given by the sum of  $E(\text{ionization}; N)$  and  $E(\text{ionization}; N^+)$ , the sum of the energies of the first and second electrons of nitrogen (Eqs. (14.88-14.89)) donated to each



double bond, the sum of  $E(\text{ionization}; O)$  and two times  $E(\text{ionization}; O^+)$ , the energies of the first and second electrons of oxygen (Eqs. (14.90-14.91)) donated to the double bonds,  $E_T(N, 2p)$ , the  $N2p$  AO contribution due to the decrease in radius with the formation of each bond (Eq. (14.93)), two times  $E_T(O, 2p)$ , the  $O2p$  AO contribution due to the decrease in radius with the formation of each bond (Eq. (14.95)), and two times  $E_T(N=O, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (14.113):

$$\begin{aligned}
 E_T(NO_2) &= \left( \begin{aligned} &E(\text{ionization}; N) + E(\text{ionization}; N^+) \\ &+ E(\text{ionization}; O) + 2E(\text{ionization}; O^+) + E_T(N, 2p) \\ &+ 2E_T(O, 2p) + 2E_T(N=O, \sigma) \end{aligned} \right) \\
 &= \left( \begin{aligned} &14.53414 \text{ eV} + 29.6013 \text{ eV} + 13.61806 \text{ eV} \\ &+ 2(35.11730 \text{ eV}) + (-10.68853) + 2(-39.92918 \text{ eV}) \\ &+ 2 \left( \frac{-e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2}}} \left( 8 \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 4 \right) \right) \end{aligned} \right) \quad (14.114) \\
 &= \left( \begin{aligned} &14.53414 \text{ eV} + 29.6013 \text{ eV} + 13.61806 \text{ eV} \\ &+ 2(35.11730 \text{ eV}) + (-10.68853) \\ &+ 2(-39.92918 \text{ eV}) + 2(-44.51329 \text{ eV}) \end{aligned} \right) \\
 &= -51.58536 \text{ eV}
 \end{aligned}$$

## VIBRATION OF $NO_2$

- 10 The vibrational energy levels of  $NO_2$  may be solved by determining the Morse potential curve from the energy relationships for the transition from a  $N$  atom and two  $O$  atoms whose parameters are given by Eqs. (10.134-10.143) and (10.154-10.163), respectively, to a  $N$  atom whose parameter  $r_s$  is given by Eq. (14.77), two  $O$  atoms whose parameter  $r_o$  is given by Eq. (14.87), and the  $\sigma$  MOs whose parameters are given by Eqs. (14.102-14.104) and (14.106.-14.107). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [4] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by
- 20 perturbation methods.

## THE DOPPLER ENERGY TERMS OF NITROGEN DIOXIDE

The equations of the radiation reaction force of nitrogen dioxide are the same as those of  $NO$  with the substitution of the  $NO_2$  parameters. Using Eq. (13.961), the angular frequency of  
 5 the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{4e^2}{4\pi\epsilon_0 a^3}} = 2.07110 \times 10^{16} \text{ rad/s} \quad (14.115)$$

where  $a$  is given by Eq. (14.102). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.07110 \times 10^{16} \text{ rad/s} = 13.63231 \text{ eV} \quad (14.116)$$

10 In Eq. (11.181), substitution of  $E_T(NO_2)/2$  for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (14.116) for  $\bar{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -25.79268 \text{ eV} \sqrt{\frac{2e(13.63231 \text{ eV})}{m_e c^2}} = -0.18840 \text{ eV} \quad (14.117)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the  
 15 transition state at their corresponding frequency. The transition state comprises  $O--NO$ , oxygen binding to  $NO$ . As in the case of  $CO_2$  bond formation, vibration in the transition state corresponds to  $\nu_3$  [5] with the maximum kinetic energy localized to the nascent  $N-O$  bond. In this case, the kinetic energy of the nuclei is the maximum for this bond. Thus,  $\bar{E}_{Kvib}$  is the vibrational energy. The decrease in the energy of the  $NO_2$  MO due to the reentrant  
 20 orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (14.117) and  $\bar{E}_{Kvib}$ , the vibrational energy. Using the experimental  $NO_2$   $E_{vib}(\nu_3)$  of  $1618 \text{ cm}^{-1}$  ( $0.20061 \text{ eV}$ ) [6] for  $\bar{E}_{Kvib}$  of the transition state,  $\bar{E}_{osc}(NO_2)$  is

$$\bar{E}_{osc}(NO_2) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + E_{vib} \quad (14.118)$$

$$25 \quad \bar{E}_{osc}(NO_2) = -0.18840 \text{ eV} + 0.20061 \text{ eV} = 0.01221 \text{ eV} \quad (14.119)$$

## TOTAL AND BOND ENERGIES OF NITROGEN DIOXIDE

$E_{T+osc}(NO_2)$ , the total energy of  $NO_2$  including the Doppler term, is given by the sum of  $E_T(NO_2)$  (Eq. (14.114)) and  $\bar{E}_{osc}(NO_2)$  given by Eq. (14.119):

$$\begin{aligned}
 E_{T+osc}(NO_2) &= \left( \begin{aligned} &2(V_e + T + V_m + V_p) + E(\text{ionization}; N) + E(\text{ionization}; N^+) \\ &+ E(\text{ionization}; O) + 2E(\text{ionization}; O^+) \\ &+ E_T(N, 2p) + 2E_T(O, 2p) + \bar{E}_{osc}(NO_2) \end{aligned} \right) \\
 &= \left( \begin{aligned} &2E_T(N = O, \sigma) + E(\text{ionization}; N) + E(\text{ionization}; N^+) \\ &+ E(\text{ionization}; O) + 2E(\text{ionization}; O^+) \\ &+ E_T(N, 2p) + 2E_T(O, 2p) + \bar{E}_{osc}(NO_2) \end{aligned} \right) \quad (14.120) \\
 &= E_T(NO_2) + \bar{E}_{osc}(NO_2)
 \end{aligned}$$

$$\begin{aligned}
 E_{T+osc}(NO_2) &= \left( \begin{aligned} &2 \left( \frac{-e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2}}} \left( 8 \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 4 \right) \right) \\ &E(\text{ionization}; N) + E(\text{ionization}; N^+) \\ &+ E(\text{ionization}; O) + 2E(\text{ionization}; O^+) \\ &- \sum_{N,n=4}^4 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_5} - \frac{1}{r_7} \right) - 2 \sum_{O,n=4}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_8} \right) \\ &\left( 1 + \frac{1}{2} \sqrt{\frac{2\hbar \sqrt{\frac{4e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} \right) + E_{vib} \end{aligned} \right) \quad (14.121) \\
 &= -51.58536 \text{ eV} - 0.18840 \text{ eV} + E_{vib}
 \end{aligned}$$

From Eqs. (14.119-14.121), the total energy of the  $NO_2$  MO is

$$\begin{aligned}
 E_{T+osc}(NO_2) &= -51.58536 \text{ eV} + \bar{E}_{osc}(NO_2) \\
 &= -51.58536 \text{ eV} + 0.01221 \text{ eV} \\
 &= -51.57315 \text{ eV} \quad (14.122)
 \end{aligned}$$

where the experimental  $E_{vib}$  was used.

As in the case of the dissociation of the bond of the hydroxyl radical, an oxygen atom  
 10 is formed with dissociation of  $NO_2$ .  $O$  has two unpaired electrons as shown in Eq. (13.55)  
 which interact to stabilize the atom as shown by Eq. (10.161-10.162). The lowering of the  
 energy of the reactants decreases the bond energy. Thus, the total energy of oxygen is

reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.101):

$$E(\text{magnetic}) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 a_0^3} = \frac{8\pi\mu_0 \mu_B^2}{a_0^3} = 0.11441 \text{ eV} \quad (14.123)$$

The  $\text{NO}_2$  bond dissociation energy,  $E_D(\text{NO}_2)$ , is given by the sum of the energies of the  
5  $\text{NO}$  and the  $\text{O}$  atom minus the sum of  $E_{T+\text{osc}}(\text{NO}_2)$  and  $E(\text{magnetic})$ :

$$E_D(\text{NO}_2) = E(\text{NO}) + E(\text{O}) - (E(\text{magnetic}) + E_{T+\text{osc}}(\text{NO}_2)) \quad (14.124)$$

The energy of an oxygen atom is given by the negative of Eq. (14.90), and  $E_T(\text{NO})$  is given by the sum of the experimental energies of  $\text{N}$  (negative of Eq. (14.88)),  $\text{O}$ , and the negative of the bond energy of  $\text{NO}$  (Eq. (13.974)):

$$10 \quad E(\text{NO}) = -14.53414 \text{ eV} - 13.618060 \text{ eV} - 6.53529 \text{ eV} = -34.68749 \text{ eV} \quad (14.125)$$

Thus, the  $\text{NO}_2$  bond dissociation energy,  $E_D(\text{NO}_2)$ , given by Eqs. (4.90) and (14.112-14.125) is

$$\begin{aligned} E_D(\text{NO}_2) &= -(34.68749 \text{ eV} + 13.618060 \text{ eV}) - (E(\text{magnetic}) + E_{T+\text{osc}}(\text{NO}_2)) \\ &= -48.30555 \text{ eV} - (0.11441 \text{ eV} - 51.57315 \text{ eV}) \\ &= 3.15319 \text{ eV} \end{aligned} \quad (14.126)$$

The experimental  $\text{NO}_2$  bond dissociation energy is [7]

$$15 \quad E_{D298}(\text{NO}_2) = 3.161 \text{ eV} \quad (14.127)$$

## BOND ANGLE OF $\text{NO}_2$

The  $\text{NO}_2$  MO comprises a linear combination of two  $\text{N}=\text{O}$ -bond MOs. A bond is also possible between the two  $\text{O}$  atoms of the  $\text{N}=\text{O}$  bonds. Such  $\text{O}=\text{O}$  bonding would  
20 decrease the  $\text{N}=\text{O}$  bond strength since electron density would be shifted from the  $\text{N}=\text{O}$  bonds to the  $\text{O}=\text{O}$  bond. Thus, the bond angle between the two  $\text{N}=\text{O}$  bonds is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal  $\text{O}$  atoms of the  $\text{N}=\text{O}$  bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the  $\text{O}=\text{O}$  ellipsoidal MO is

$$25 \quad c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \quad (14.128)$$

The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \quad (14.129)$$

The length of the semiminor axis of the prolate spheroidal  $O=O$  MO  $b=c$  is given by Eq. (13.167).

The component energies and the total energy  $E_T$  of the  $O=O$  bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of  $H_2$  except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the  $O=O$  double bond with two pairs of paired electrons. Substitution of Eq. (14.128) into Eqs. (11.207-11.212) gives

$$0 = \left[ \frac{-e^2}{8\pi\epsilon_0\sqrt{\frac{aa_0}{2}}} \left( 8 \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 4 \right) \left[ 1 + \sqrt{\frac{4e^2}{4\pi\epsilon_0 a^3} \frac{m_e}{m_e c^2}} \right] + \frac{1}{2} \hbar \sqrt{\frac{4e^2}{8\pi\epsilon_0 a^3} - \frac{4e^2}{8\pi\epsilon_0 (a+c')^3}} \frac{1}{8m_p} \right] \quad (14.130)$$

From the energy relationship given by Eq. (14.130) and the relationship between the axes given by Eqs. (14.128-14.129) and (13.167-14.168), the dimensions of the  $O=O$  MO can be solved.

The most convenient way to solve Eq. (14.130) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 8.3360a_0 = 4.4112 \times 10^{-10} \text{ m} \quad (14.131)$$

Substitution of Eq. (14.131) into Eq. (14.128) gives

$$c' = 2.0416a_0 = 1.0804 \times 10^{-10} \text{ m} \quad (14.132)$$

The internuclear distance given by multiplying Eq. (14.132) by two is

$$2c' = 4.0831a_0 = 2.1607 \times 10^{-10} \text{ m} \quad (14.133)$$

Substitution of Eqs. (14.131-14.132) into Eq. (14.167) gives

$$b = c = 8.0821a_0 = 4.2769 \times 10^{-10} \text{ m} \quad (14.134)$$

Substitution of Eqs. (14.131-14.132) into Eq. (14.168) gives

$$e = 0.2449 \quad (14.135)$$

From,  $2c'_{c=c}$  (Eq. (14.133)), the distance between the two  $O$  atoms when the total energy of the corresponding MO is zero (Eq. (14.130)), and  $2c'_{N=O}$  (Eq. (14.104)), the

internuclear distance of each  $N = O$  bond, the corresponding bond angle can be determined from the law of cosines. Using, Eqs. (13.240-13.242), the bond angle  $\theta$  between the  $N = O$  bonds is

$$\begin{aligned}\theta &= \cos^{-1} \left( \frac{2(2.24347)^2 - (4.0831)^2}{2(2.24347)^2} \right) \\ &= \cos^{-1}(-0.6562) \\ &= 131.012^\circ\end{aligned}\tag{14.136}$$

5 The experimental angle between the  $N = O$  bonds is [3]

$$\theta = 134.1^\circ\tag{14.137}$$

The results of the determination of bond parameters of  $NO_2$  are given in Table 14.1.

The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and

10 calculated results is excellent.

## ETHANE MOLECULE ( $CH_3CH_3$ )

The ethane molecule  $CH_3CH_3$  is formed by the reaction of two methyl radicals:



15  $CH_3CH_3$  can be solved using the same principles as those used to solve  $CH_3$ , wherein the  $2s$  and  $2p$  shells of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. First, two sets of three  $H$  atomic orbitals (AOs) combine with two sets of three

20 carbon  $2sp^3$  HOs to form two methyl groups comprising a linear combination of six diatomic  $H_2$ -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. Then, the two  $CH_3$  groups bond by forming a  $H_2$ -type MO between the remaining  $C2sp^3$  HO on each carbon.

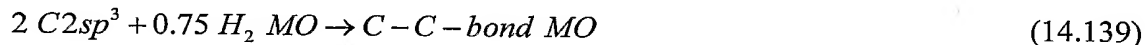
## 25 FORCE BALANCE OF THE $C - C$ -BOND MO OF ETHANE

$CH_3CH_3$  comprises a chemical bond between two  $CH_3$  radicals wherein each methyl radical comprises three chemical bonds between carbon and hydrogen atoms. The solution of the parameters of  $CH_3$  is given in the Methyl Radical ( $CH_3$ ) section. Each  $C - H$  bond of

$CH_3$  having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75%  $H_2$ -type ellipsoidal MO and 25%  $C2sp^3$  HO. The proton of the  $H$  atom and the nucleus of the  $C$  atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , each of the three  $C-H$ -bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the  $H$  proton that is continuous with the  $C2sp^3$  shell at the  $C$  atom whose nucleus serves as the other focus. The electron configuration and the energy,  $E(C, 2sp^3)$ , of the  $C2sp^3$  shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of each  $C-H$  bond is provided by the spin-pairing force of the  $CH_3$  MO that has the symmetry of an  $s$  orbital that superimposes with the  $C2sp^3$  orbitals such that the corresponding angular momenta are unchanged.

Two  $CH_3$  radicals bond to form  $CH_3CH_3$  by forming a MO between the two remaining  $C2sp^3$ -HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between two  $C2sp^3$  HOs to form a molecular orbital (MO) comprising two spin-paired electrons permits each  $C2sp^3$  HO to decrease in radius and energy.

As in the case of the  $C-H$  bonds, the  $C-C$ -bond MO is a prolate-spheroidal-MO surface that cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the  $C2sp^3$  shell at each  $C$  atom. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the  $C2sp^3$  shell. As in the case of previous examples of energy-matched MOs such as those of  $OH$ ,  $NH$ ,  $CH$ , and the  $C=O$ -bond MO of  $CO_2$ , the  $C-C$ -bond MO of ethane must comprise 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $C-C$ -bond MO must comprise two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the two  $C2sp^3$  HOs:



The linear combination of the  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution from each  $C2sp^3$  HO to the  $C-C$ -bond MO to achieve an energy minimum. The force balance of the  $C-C$ -bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.139) and the energy matching condition between the  $C2sp^3$ -HO components of the MO.

Similarly, the energies of each  $CH_3$  MO involve each  $C2sp^3$  and each  $H1s$  electron with the formation of each  $C-H$  bond. The sum of the energies of the  $H_2$ -type ellipsoidal MOs is matched to that of the  $C2sp^3$  shell. This energy is determined by the considering the effect of the donation of 25% electron density from the two  $C2sp^3$  HOs to the  $C-C$ -bond MO. The  $2sp^3$  hybridized orbital arrangement given by Eq. (13.422) is

$$\begin{array}{cccc} & & 2sp^3 \text{ state} & \\ \uparrow & \uparrow & \uparrow & \uparrow \\ \hline 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \quad (14.140)$$

15

where the quantum numbers  $(\ell, m_\ell)$  are below each electron. The total energy of the state is given by the sum over the four electrons. The sum  $E_T(C, 2sp^3)$  of calculated energies of  $C$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$\begin{aligned} E_T(C, 2sp^3) &= 64.3921 \text{ eV} + 48.3125 \text{ eV} + 24.2762 \text{ eV} + 11.27671 \text{ eV} \\ &= 148.25751 \text{ eV} \end{aligned} \quad (14.141)$$

which agrees well with the sum of  $148.02532 \text{ eV}$  from the experimental [2] values. Consider the case of the  $C2sp^3$  HO of each methyl radical. The orbital-angular-momentum interactions cancel such that the energy of the  $E_T(C, 2sp^3)$  is purely Coulombic. By considering that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{2sp^3}$  of the  $C2sp^3$  shell may be calculated from the Coulombic energy using Eq. (10.102):

$$r_{2sp^3} = \sum_{n=2}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0 (e148.25751 \text{ eV})} = \frac{10e^2}{8\pi\epsilon_0 (e148.25751 \text{ eV})} = 0.91771a_0 \quad (14.142)$$



where  $Z = 6$  for carbon. Using Eqs. (10.102) and (14.142), the Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E_{Coulomb}(C, 2sp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{2sp^3}} = \frac{-e^2}{8\pi\epsilon_0 0.91771a_0} = -14.82575 \text{ eV} \quad (14.143)$$

During hybridization, one of the spin-paired  $2s$  electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152) at the initial radius of the  $2s$  electrons. From Eq. (10.62) with  $Z = 6$ , the radius  $r_3$  of  $C2s$  shell is

$$r_3 = 0.84317a_0 \quad (14.144)$$

Using Eqs. (13.152) and (14.144), the unpairing energy is

$$E(\text{magnetic}) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} = \frac{8\pi\mu_0 \mu_B^2}{(0.84317a_0)^3} = 0.19086 \text{ eV} \quad (14.145)$$

Using Eqs. (14.143) and (14.145), the energy  $E(C, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$\begin{aligned} E(C, 2sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{2sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} \\ &= -14.82575 \text{ eV} + 0.19086 \text{ eV} \\ &= -14.63489 \text{ eV} \end{aligned} \quad (14.146)$$

Next, consider the formation of the  $C-C$ -bond MO of ethane from two methyl radicals, each having a  $C2sp^3$  electron with an energy given by Eq. (14.146). The total energy of the state is given by the sum over the four electrons. The sum  $E_T(C_{ethane}, 2sp^3)$  of calculated energies of  $C2sp^3$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$\begin{aligned} E_T(C_{ethane}, 2sp^3) &= -(64.3921 \text{ eV} + 48.3125 \text{ eV} + 24.2762 \text{ eV} + E(C, 2sp^3)) \\ &= -(64.3921 \text{ eV} + 48.3125 \text{ eV} + 24.2762 \text{ eV} + 14.63489 \text{ eV}) \\ &= -151.61569 \text{ eV} \end{aligned} \quad (14.147)$$

where  $E(C, 2sp^3)$  is the sum of the energy of  $C$ ,  $-11.27671 \text{ eV}$ , and the hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the  $E_T(C_{ethane}, 2sp^3)$  is purely Coulombic.

The sharing of electrons between two  $C2sp^3$  HOs to form a  $C-C$ -bond MO permits

each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each  $C2sp^3$  HO donates an excess of 25% of its electron density to the  $C-C$ -bond MO to form an energy minimum. By considering this electron redistribution in the ethane molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{ethane2sp^3}$  of the  $C2sp^3$  shell of ethane may be calculated from the Coulombic energy using Eq. (10.102):

$$\begin{aligned} r_{ethane2sp^3} &= \left( \sum_{n=2}^5 (Z-n) - 0.25 \right) \frac{e^2}{8\pi\epsilon_0 (e151.61569 \text{ eV})} \\ &= \frac{9.75e^2}{8\pi\epsilon_0 (e151.61569 \text{ eV})} \\ &= 0.87495a_0 \end{aligned} \quad (14.148)$$

Using Eqs. (10.102) and (14.148), the Coulombic energy  $E_{Coulomb}(C_{ethane}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$\begin{aligned} E_{Coulomb}(C_{ethane}, 2sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{ethane2sp^3}} \\ &= \frac{-e^2}{8\pi\epsilon_0 0.87495a_0} \\ &= -15.55033 \text{ eV} \end{aligned} \quad (14.149)$$

During hybridization, one of the spin-paired  $2s$  electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152). Using Eqs. (14.145) and (14.149), the energy  $E(C_{ethane}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$\begin{aligned} E(C_{ethane}, 2sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{ethane2sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} \\ &= -15.55033 \text{ eV} + 0.19086 \text{ eV} \\ &= -15.35946 \text{ eV} \end{aligned} \quad (14.150)$$

Thus,  $E_T(C-C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell with the formation of the  $C-C$ -bond MO is given by the difference between Eq. (14.146) and Eq. (14.150):

$$\begin{aligned} E_T(C-C, 2sp^3) &= E(C_{ethane}, 2sp^3) - E(C, 2sp^3) \\ &= -15.35946 \text{ eV} - (-14.63489 \text{ eV}) \\ &= -0.72457 \text{ eV} \end{aligned} \quad (14.151)$$

The  $H_2$ -type ellipsoidal MO comprises 75% of the  $C-C$ -bond MO shared between two  $C2sp^3$  HOs corresponding to the electron charge density in Eq. (11.65) of  $\frac{-0.75e}{2}$ . But, the additional 25% charge-density contribution to the  $C-C$ -bond MO causes the electron charge density in Eq. (11.65) to be given by  $\frac{-e}{2} = -0.5e$ . Thus, the force constant  $k'$  to

5 determine the ellipsoidal parameter  $c'$  in terms of the central force of the foci given by Eq. (11.65) is

$$k' = \frac{(0.5)2e^2}{4\pi\epsilon_0} \quad (14.152)$$

The distance from the origin to each focus  $c'$  is given by substitution of Eq. (14.152) into Eq. (13.60). Thus, the distance from the origin of the  $C-C$ -bond MO to each focus  $c'$  is given

10 by

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 a}} = \sqrt{aa_0} \quad (14.153)$$

The internuclear distance from Eq. (14.153) is

$$2c' = 2\sqrt{aa_0} \quad (14.154)$$

The length of the semiminor axis of the prolate spheroidal  $C-C$ -bond MO  $b = c$  is given by

15 Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of the  $C-C$ -bond MO. Since the  $C-C$ -bond MO comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $C_{ethane} 2sp^3$  HO of each carbon, the energy  $E(C_{ethane}, 2sp^3)$  in Eq. (14.150) adds to that of the  $H_2$ -type ellipsoidal MO to give the total energy of the  $C-C$ -bond MO.

20 From the energy equation and the relationship between the axes, the dimensions of the  $C-C$ -bond MO are solved. Similarly,  $E(C_{ethane}, 2sp^3)$  is added to the energy of the  $H_2$ -type ellipsoidal MO of each  $C-H$  bond of the methyl groups to give its total energy. From the energy equation and the relationship between the axes, the dimensions of the equivalent  $C-H$ -bond MOs of the methyl groups in ethane are solved.

25 The general equations for the energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  of the  $C-C$ -bond MO are the same as those of the  $CH$  MO as well as each  $C-H$ -bond MO of the methyl groups except that energy of the  $C_{ethane} 2sp^3$  HO is used. Since the prolate

spheroidal  $H_2$ -type MO transitions to the  $C_{ethane} 2sp^3$  HO of each carbon and the energy of the  $C_{ethane} 2sp^3$  shell must remain constant and equal to the  $E(C_{ethane}, 2sp^3)$  given by Eq. (14.150), the total energy  $E_T(C-C, \sigma)$  of the  $\sigma$  component of the  $C-C$ -bond MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C_{ethane} 2sp^3$  HO and the  $H_2$ -type ellipsoidal MO that forms the  $\sigma$  component of the  $C-C$ -bond MO as given by Eq. (14.139) with the electron charge redistribution. Using Eqs. (13.431) and (14.150),  $E_T(C-C, \sigma)$  is given by

$$E_T(C-C, \sigma) = E_T + E(C_{ethane}, 2sp^3) \\ = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.35946 \text{ eV} \quad (14.155)$$

To match the boundary condition that the total energy of the entire the  $H_2$ -type ellipsoidal MO is given by Eqs. (11.212) and (13.75),  $E_T(C-C, \sigma)$  given by Eq. (14.155) is set equal to Eq. (13.75):

$$E_T(C-C, \sigma) = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.35946 \text{ eV} \\ = -31.63536831 \text{ eV} \quad (14.156)$$

From the energy relationship given by Eq. (14.156) and the relationship between the axes given by Eqs. (14.153-14.154) and (13.62-13.63), the dimensions of the  $C-C$ -bond MO can be solved.

Substitution of Eq. (14.153) into Eq. (14.156) gives

$$\frac{e^2}{8\pi\epsilon_0 \sqrt{aa_0}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}} - 1 \right] = e16.27589 \quad (14.157)$$

The most convenient way to solve Eq. (14.157) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 2.10725a_0 = 1.11511 \times 10^{-10} \text{ m} \quad (14.158)$$

Substitution of Eq. (14.158) into Eq. (14.153) gives

$$c' = 1.45164a_0 = 7.68173 \times 10^{-11} \text{ m} \quad (14.159)$$

The internuclear distance given by multiplying Eq. (14.159) by two is

$$2c' = 2.90327a_0 = 1.53635 \times 10^{-10} \text{ m} \quad (14.160)$$

The experimental bond distance is [3]

$$2c' = 1.5351 \times 10^{-10} \text{ m} \quad (14.161)$$

Substitution of Eqs. (14.158-14.159) into Eq. (13.62) gives

$$b = c = 1.52750a_0 = 8.08317 \times 10^{-11} \text{ m} \quad (14.162)$$

Substitution of Eqs. (14.158-14.159) into Eq. (13.63) gives

$$5 \quad e = 0.68888 \quad (14.163)$$

The nucleus of the  $C$  atoms comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{ethane} 2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{ethane 2sp^3} = 0.87495a_0$  is the radius of the  $C_{ethane} 2sp^3$  shell.

10 Substitution of Eqs. (14.158-14.159) into Eq. (13.261) gives

$$\theta' = 67.33^\circ \quad (14.164)$$

Then, the angle  $\theta_{C-C_{ethane} 2sp^3 HO}$  the radial vector of the  $C 2sp^3$  HO makes with the internuclear axis is

$$\theta_{C-C_{ethane} 2sp^3 HO} = 180^\circ - 67.33^\circ = 112.67^\circ \quad (14.165)$$

15 as shown in Figure 37.

Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-C_{ethane}, H_2 MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -

20 type ellipsoidal MO with the  $C_{ethane} 2sp^3$  radial vector obeys the following relationship:

$$r_{ethane 2sp^3} \sin \theta_{C-C_{ethane} 2sp^3 HO} = 0.87495a_0 \sin \theta_{C-C_{ethane} 2sp^3 HO} = b \sin \theta_{C-C_{ethane}, H_2 MO} \quad (14.166)$$

such that

$$\theta_{C-C_{ethane}, H_2 MO} = \sin^{-1} \frac{0.87495a_0 \sin \theta_{C-C_{ethane} 2sp^3 HO}}{b} = \sin^{-1} \frac{0.87495a_0 \sin 112.67^\circ}{b} \quad (14.167)$$

with the use of Eq. (14.166). Substitution of Eq. (14.162) into Eq. (14.167) gives

$$25 \quad \theta_{C-C_{ethane}, H_2 MO} = 31.91^\circ \quad (14.168)$$

Then, the distance  $d_{C-C_{ethane}, H_2 MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-C_{ethane}, H_2 MO} = a \cos \theta_{C-C_{ethane}, H_2 MO} \quad (14.169)$$

Substitution of Eqs. (14.158) and (14.168) into Eq. (14.169) gives

$$d_{C-C_{ethane}, H_2MO} = 1.78885a_0 = 9.46617 \times 10^{-11} m \quad (14.170)$$

The distance  $d_{C-C_{ethane} 2sp^3 HO}$  along the internuclear axis from the origin of the  $C$  atom to the point of intersection of the orbitals is given by

$$d_{C-C_{ethane} 2sp^3 HO} = d_{C-C_{ethane}, H_2MO} - c' \quad (14.171)$$

5 Substitution of Eqs. (14.159) and (14.170) into Eq. (14.171) gives

$$d_{C-C_{ethane} 2sp^3 HO} = 0.33721a_0 = 1.78444 \times 10^{-11} m \quad (14.172)$$

### FORCE BALANCE OF THE $CH_3$ MOs OF ETHANE

Each of the two equivalent  $CH_3$  MOs must comprise three  $C-H$  bonds with each  
10 comprising 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO as given by Eq. (13.540):

$$3[1 C2sp^3 + 0.75 H_2 MO] \rightarrow CH_3 MO \quad (14.173)$$

The force balance of the  $CH_3$  MO is determined by the boundary conditions that arise from  
15 the linear combination of orbitals according to Eq. (13.540) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant  $k'$  to determine the ellipsoidal parameter  $c'$  of the each  $H_2$ -type-ellipsoidal-MO component of the  $CH_3$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each  $C-H$ -bond MO to each focus  $c'$  is  
20 given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal  $C-H$ -bond MO  $b = c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of each  $C-H$ -bond MO. Since each of the three prolate spheroidal  $C-H$ -bond MOs comprises an  $H_2$ -type-  
25 ellipsoidal MO that transitions to the  $C_{ethane} 2sp^3$  HO of ethane, the energy  $E(C_{ethane}, 2sp^3)$  of Eq. (14.150) adds to that of the three corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $CH_3$  MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH_3$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ ,  $T$ , and  $V_m$  are the same as those of methyl radical, three times those of  $CH$  corresponding to the three  $C-H$  bonds except that energy of the  $C_{ethane} 2sp^3$  HO is used. Since the each prolate spheroidal  $H_2$ -type MO transitions to the  $C_{ethane} 2sp^3$  HO and the energy of the  $C_{ethane} 2sp^3$  shell must remain constant and equal to the  $E(C_{ethane}, 2sp^3)$  given by Eq. (14.150), the total energy  $E_{T_{ethane}}(CH_3)$  of the  $CH_3$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C_{ethane} 2sp^3$  HO and the three  $H_2$ -type ellipsoidal MOs that forms the  $CH_3$  MO as given by Eq. (13.540). Using Eq. (13.431),  $E_{T_{ethane}}(CH_3)$  is given by

$$\begin{aligned} E_{T_{ethane}}(CH_3) &= E_T + E(C_{ethane}, 2sp^3) \\ &= -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.35946 \text{ eV} \end{aligned} \quad (14.174)$$

$E_{T_{ethane}}(CH_3)$  given by Eq. (14.174) is set equal to three times the energy of the  $H_2$ -type ellipsoidal MO minus two times the Coulombic energy of  $H$  given by Eq. (13.542):

$$E_T(CH_3) = -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.35946 \text{ eV} = -67.69450 \text{ eV} \quad (14.175)$$

From the energy relationship given by Eq. (14.175) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH_3$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.175) gives

$$\frac{3e^2}{8\pi\epsilon_0 \sqrt{\frac{2aa_0}{3}}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right] = e52.33505 \quad (14.176)$$

The most convenient way to solve Eq. (14.176) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.64469a_0 = 8.70331 \times 10^{-11} \text{ m} \quad (14.177)$$

Substitution of Eq. (14.177) into Eq. (14.60) gives

$$c' = 1.04712a_0 = 5.54111 \times 10^{-11} \text{ m} \quad (14.178)$$

The internuclear distance given by multiplying Eq. (14.178) by two is

$$2c' = 2.09424a_0 = 1.10822 \times 10^{-10} \text{ m} \quad (14.179)$$

The experimental bond distance is [3]

$$2c' = 1.0940 \times 10^{-10} \text{ m} \quad (14.180)$$

Substitution of Eqs. (14.177-14.178) into Eq. (14.62) gives

$$b = c = 1.26828a_0 = 6.71145 \times 10^{-11} \text{ m} \quad (14.181)$$

Substitution of Eqs. (14.177-14.178) into Eq. (14.63) gives

$$5 \quad e = 0.63667 \quad (14.182)$$

The nucleus of the  $H$  atom and the nucleus of the  $C$  atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{ethane} 2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{ethane 2sp^3} = 0.87495a_0$  is

10 the radius of the  $C_{ethane} 2sp^3$  shell. Substitution of Eqs. (14.177-14.178) into Eq. (13.261) gives

$$\theta' = 79.34^\circ \quad (14.183)$$

Then, the angle  $\theta_{C-H_{ethane} 2sp^3 HO}$  the radial vector of the  $C 2sp^3$  HO makes with the internuclear axis is

$$15 \quad \theta_{C-H_{ethane} 2sp^3 HO} = 180^\circ - 79.34^\circ = 100.66^\circ \quad (14.184)$$

as shown in Figure 38.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-H_{ethane}, H_2 MO}$  between the  
20 internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{ethane} 2sp^3$  radial vector obeys the following relationship:

$$r_{ethane 2sp^3} \sin \theta_{C-H_{ethane} 2sp^3 HO} = 0.87495a_0 \sin \theta_{C-H_{ethane} 2sp^3 HO} = b \sin \theta_{C-H_{ethane}, H_2 MO} \quad (14.185)$$

such that

$$\theta_{C-H_{ethane}, H_2 MO} = \sin^{-1} \frac{0.87495a_0 \sin \theta_{C-H_{ethane} 2sp^3 HO}}{b} = \sin^{-1} \frac{0.87495a_0 \sin 100.66^\circ}{b} \quad (14.186)$$

25 with the use of Eq. (14.184). Substitution of Eq. (14.181) into Eq. (14.186) gives

$$\theta_{C-H_{ethane}, H_2 MO} = 42.68^\circ \quad (14.187)$$

Then, the distance  $d_{C-H_{ethane}, H_2 MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{ethane}, H_2 MO} = a \cos \theta_{C-H_{ethane}, H_2 MO} \quad (14.188)$$



Substitution of Eqs. (14.177) and (14.187) into Eq. (14.188) gives

$$d_{C-H_{ethane}, H_2MO} = 1.20901a_0 = 6.39780 \times 10^{-11} \text{ m} \quad (14.189)$$

The distance  $d_{C-H_{ethane} 2sp^3HO}$  along the internuclear axis from the origin of the  $C$  atom to the point of intersection of the orbitals is given by

$$5 \quad d_{C-H_{ethane} 2sp^3HO} = d_{C-H_{ethane}, H_2MO} - c' \quad (14.190)$$

Substitution of Eqs. (14.178) and (14.189) into Eq. (14.190) gives

$$d_{C-H_{ethane} 2sp^3HO} = 0.16189a_0 = 8.56687 \times 10^{-12} \text{ m} \quad (14.191)$$

### BOND ANGLE OF THE $CH_3$ GROUPS

- 10 Each  $CH_3$  MO comprises a linear combination of three  $C-H$ -bond MOs. Each  $C-H$ -bond MO comprises the superposition of a  $H_2$ -type ellipsoidal MO and the  $C_{ethane} 2sp^3$  HO. A bond is also possible between the two H atoms of the  $C-H$  bonds. Such  $H-H$  bonding would decrease the  $C-H$  bond strength since electron density would be shifted from the  $C-H$  bonds to the  $H-H$  bond. Thus, the bond angle between the two  $C-H$  bonds is
- 15 determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal H atoms of the  $C-H$  bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the  $H-H$  ellipsoidal MO is

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \quad (14.192)$$

The internuclear distance from Eq. (13.229) is

$$20 \quad 2c' = 2\sqrt{\frac{aa_0}{2}} \quad (14.193)$$

The length of the semiminor axis of the prolate spheroidal  $H-H$  MO  $b = c$  is given by Eq. (14.62).

- The bond angle of the  $CH_3$  groups of ethane is derived by using the orbital composition and an energy matching factor as in the case with the  $CH_3$  radical. Since the
- 25 two  $H_2$ -type ellipsoidal MOs initially comprise 75% of the  $H$  electron density of  $H_2$  and the energy of each  $H_2$ -type ellipsoidal MO is matched to that of the  $C_{ethane} 2sp^3$  HO, the component energies and the total energy  $E_T$  of the  $H-H$  bond are given by Eqs. (13.67-13.73) except that  $V_e$ ,  $T$ , and  $V_m$  are corrected for the hybridization-energy-matching factor

of 0.87495. Hybridization with 25% electron donation to the  $C-C$ -bond gives rise to the  $C_{ethane} 2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(C_{ethane}, 2sp^3)$  given by Eq. (14.149). The corresponding normalization factor for determining the zero of the total  $H-H$  bond energy is given by the ratio of 15.55033 eV, the magnitude of  $E_{Coulomb}(C_{ethane}, 2sp^3)$  given by Eq. (14.149), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). The hybridization energy factor  $C_{ethaneC2sp^3HO}$  is

$$C_{ethaneC2sp^3HO} = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{ethane2sp^3}}} = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 0.87495 a_0}} = \frac{13.605804 \text{ eV}}{15.55033 \text{ eV}} = 0.87495 \quad (14.194)$$

Substitution of Eq. (14.152) into Eq. (13.233) with the hybridization factor of 0.87495 gives

$$0 = \left[ \frac{-e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2}}} \left[ (0.87495)^{-1} \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 a^3}}}}{m_e c^2} \right] \right. \\ \left. + \hbar \sqrt{\frac{\frac{0.75e^2}{8\pi\epsilon_0 a^3} - \frac{e^2}{8\pi\epsilon_0 (a+c')^3}}{0.5m_p}} \right] \quad (14.195)$$

From the energy relationship given by Eq. (14.195) and the relationship between the axes given by Eqs. (14.192-14.193) and (14.62-14.63), the dimensions of the  $H-H$  MO can be solved.

The most convenient way to solve Eq. (14.195) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 5.7000a_0 = 3.0163 \times 10^{-10} \text{ m} \quad (14.196)$$

Substitution of Eq. (14.196) into Eq. (14.192) gives

$$c' = 1.6882a_0 = 8.9335 \times 10^{-11} \text{ m} \quad (14.197)$$

The internuclear distance given by multiplying Eq. (14.197) by two is

$$2c' = 3.3764a_0 = 1.7867 \times 10^{-10} \text{ m} \quad (14.198)$$

Substitution of Eqs. (14.196-14.197) into Eq. (14.62) gives

$$b = c = 5.4443a_0 = 2.8810 \times 10^{-10} \text{ m} \quad (14.199)$$

Substitution of Eqs. (14.196-14.197) into Eq. (14.63) gives

$$e = 0.2962 \quad (14.200)$$

From,  $2c'_{H-H}$  (Eq. (14.198)), the distance between the two  $H$  atoms when the total energy of the corresponding MO is zero (Eq. (14.195)), and  $2c'_{C-H}$  (Eq. (14.179)), the internuclear distance of each  $C-H$  bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle  $\theta$  between the  $C-H$  bonds is

$$\theta = \cos^{-1} \left( \frac{2(2.09424)^2 - (3.3764)^2}{2(2.09424)^2} \right) = \cos^{-1}(-0.29964) = 107.44^\circ \quad (14.201)$$

The experimental angle between the  $C-H$  bonds is [8]

$$\theta = 107.4^\circ \quad (14.202)$$

10 The  $CH_3$  radical has a pyramidal structure with the carbon atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. The distance  $d_{origin-H}$  from the origin to the nucleus of a hydrogen atom given by Eqs. (14.198) and (13.412) is

$$d_{origin-H} = 1.94936a_0 \quad (14.203)$$

The height along the z-axis of the pyramid from the origin to  $C$  nucleus  $d_{height}$  given by Eqs. (13.414), (14.179), and (14.203) is

$$d_{height} = 0.76540a_0 \quad (14.204)$$

The angle  $\theta_v$  of each  $C-H$  bond from the z-axis given by Eqs. (13.416), (14.203), and (14.204) is

$$\theta_v = 68.563^\circ \quad (14.205)$$

20 The  $C-C$  bond is along the z-axis. Thus, the bond angle  $\theta_{C-C-H}$  between the internuclear axis of the  $C-C$  bond and a  $H$  atom of the methyl groups is given by

$$\theta_{C-C-H} = 180 - \theta_v \quad (14.206)$$

Substitution of Eq. (14.205) into Eq. (14.206) gives

$$\theta_{C-C-H} = 111.44^\circ \quad (14.207)$$

25 The experimental angle between the  $C-C-H$  bonds is [3]

$$\theta_{C-C-H} = 111.17^\circ \quad (14.208)$$

The  $CH_3CH_3$  MO shown in Figure 39 was rendered using these parameters. A minimum energy is obtained with a staggered configuration consistent with observations [3].

The charge-density in the  $C-C$ -bond MO is increased by a factor of 0.25 with the formation of the  $C_{ethane}2sp^3$  HOs each having a smaller radius. Using the orbital composition of the  $CH_3$  groups (Eq. (14.173)) and the  $C-C$ -bond MO (Eq. (14.139), the radii of  $C1s = 0.17113a_0$  (Eq. (10.51)) and  $C_{ethane}2sp^3 = 0.87495a_0$  (Eq. (14.148)) shells, and the parameters of the  $C-C$ -bond (Eqs. (13.3-13.4), (14.158-14.160), and (14.162-14.172)), the parameters of the  $C-H$ -bond MOs (Eqs. (13.3-13.4), (14.177-14.179), and (14.181-14.191)), and the bond-angle parameters (Eqs. (14.195-14.208)), the charge-density of the  $CH_3CH_3$  MO comprising the linear combination of two sets of three  $C-H$ -bond MOs and a  $C-C$ -bond MO bridging the two methyl groups is shown in Figure 39. Each  $C-H$ -bond MO comprises a  $H_2$ -type ellipsoidal MO and a  $C_{ethane}2sp^3$  HO having the dimensional diagram shown in Figure 38. The  $C-C$ -bond MO comprises a  $H_2$ -type ellipsoidal MO bridging two  $C_{ethane}2sp^3$  HOs having the dimensional diagram shown in Figure 37.

### ENERGIES OF THE $CH_3$ GROUPS

The energies of each  $CH_3$  group of ethane are given by the substitution of the semiprincipal axes (Eqs. (14.177-14.178) and (14.181)) into the energy equations of the methyl radical (Eqs. (13.556-13.560)), with the exception that  $E(C_{ethane}, 2sp^3)$  replaces  $E(C, 2sp^3)$  in Eq. (13.560):

$$V_e = 3(0.91771) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -107.68424 \text{ eV} \quad (14.209)$$

$$V_p = \frac{3e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 38.98068 \text{ eV} \quad (14.210)$$

$$T = 3(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 32.73700 \text{ eV} \quad (14.211)$$

$$V_m = 3(0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.36850 \text{ eV} \quad (14.212)$$

$$E_{T_{ethane}}(CH_3) = -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.35946 \text{ eV} = -67.69451 \text{ eV} \quad (14.213)$$

where  $E_{T_{ethane}}(CH_3)$  is given by Eq. (14.174) which is reiteratively matched to Eq. (13.542) within five-significant-figure round off error.

## VIBRATION OF THE $^{12}\text{CH}_3$ GROUPS

The vibrational energy levels of  $\text{CH}_3$  in ethane may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and  
 5 the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $^{12}\text{CH}_3$ GROUPS

- 10 The equations of the radiation reaction force of the methyl groups in ethane are the same as those of the methyl radical with the substitution of the methyl-group parameters. Using Eq. (13.561), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 2.50664 \times 10^{16} \text{ rad/s} \quad (14.214)$$

- where  $b$  is given by Eq. (14.181). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq.  
 15 (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.50664 \times 10^{16} \text{ rad/s} = 16.49915 \text{ eV} \quad (14.215)$$

- In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (14.215) for  $\bar{E}_K$  gives the Doppler energy of the electrons of each of the  
 20 three bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(16.49915 \text{ eV})}{m_e c^2}} = -0.25422 \text{ eV} \quad (14.216)$$

- In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $\text{CH}_3$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic  
 25 oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (14.216) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which

is  $1/2$  of the vibrational energy of each  $C-H$  bond. Using  $\omega_e$  given by Eq. (13.458) for  $\bar{E}_{Kvib}$  of the transition state having three independent bonds,  $\bar{E}'_{ethane\ osc} (^{12}CH_3)$  per bond is

$$\bar{E}'_{ethane\ osc} (^{12}CH_3) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (14.217)$$

$$\bar{E}'_{ethane\ osc} (^{12}CH_3) = -0.25422\ eV + \frac{1}{2} (0.35532\ eV) = -0.07656\ eV \quad (14.218)$$

5 Given that the vibration and reentrant oscillation is for three  $C-H$  bonds,  $\bar{E}_{ethane\ osc} (^{12}CH_3)$ , is:

$$\begin{aligned} \bar{E}_{ethane\ osc} (^{12}CH_3) &= 3 \left( \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \\ &= 3 \left( -0.25422\ eV + \frac{1}{2} (0.35532\ eV) \right) \\ &= -0.22967\ eV \end{aligned} \quad (14.219)$$

### TOTAL AND DIFFERENCE ENERGIES OF THE $^{12}CH_3$ GROUPS

10  $E_{ethaneT+osc} (^{12}CH_3)$ , the total energy of each  $^{12}CH_3$  group including the Doppler term, is given by the sum of  $E_{T_{ethane}} (CH_3)$  (Eq. (14.213)) and  $\bar{E}_{ethane\ osc} (^{12}CH_3)$  given by Eq. (14.219):

$$\begin{aligned} E_{ethaneT+osc} (CH_3) &= V_e + T + V_m + V_p + E(C_{ethane}, 2sp^3) + \bar{E}_{ethane\ osc} (^{12}CH_3) \\ &= E_{T_{ethane}} (CH_3) + \bar{E}_{ethane\ osc} (^{12}CH_3) \end{aligned} \quad (14.220)$$

$$\begin{aligned} E_{ethaneT+osc} (^{12}CH_3) &= \left\{ \left( \frac{-3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.359469\ eV \right) \right. \\ &\quad \left. - 3 \left( (31.63536831\ eV) \sqrt{\frac{2\hbar \sqrt{\frac{3}{4} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2}} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \right\} \\ &= -67.69450\ eV - 3 \left( 0.25422\ eV - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \end{aligned} \quad (14.221)$$

From Eqs. (14.217-14.221), the total energy of each  $^{12}CH_3$  is

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$$\begin{aligned}
 E_{ethaneT+osc}({}^{12}CH_3) &= -67.69450 \text{ eV} + \bar{E}_{ethane\ osc}({}^{12}CH_3) \\
 &= -67.69450 \text{ eV} - 3 \left( 0.25422 \text{ eV} - \frac{1}{2} (0.35532 \text{ eV}) \right) \\
 &= -67.92417 \text{ eV}
 \end{aligned} \tag{14.222}$$

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

The total energy for each methyl radical given by Eq. (13.569) is

$$\begin{aligned}
 E_{radicalT+osc}({}^{12}CH_3) &= -67.69450 \text{ eV} + \bar{E}_{radical\ osc}({}^{12}CH_3) \\
 &= -67.69450 \text{ eV} - 3 \left( 0.25670 \text{ eV} - \frac{1}{2} (0.35532 \text{ eV}) \right) \\
 &= -67.93160 \text{ eV}
 \end{aligned} \tag{14.223}$$

- 5 The difference in energy between the methyl groups and the methyl radical  $\Delta E_{T+osc}({}^{12}CH_3)$  is given by two times the difference between Eqs. (14.222) and (14.223):

$$\begin{aligned}
 \Delta E_{T+osc}({}^{12}CH_3) &= 2 \left( E_{ethaneT+osc}({}^{12}CH_3) - E_{radicalT+osc}({}^{12}CH_3) \right) \\
 &= 2 \left( -67.92417 \text{ eV} - (-67.93160 \text{ eV}) \right) \\
 &= 0.01487 \text{ eV}
 \end{aligned} \tag{14.224}$$

## SUM OF THE ENERGIES OF THE C-C $\sigma$ MO AND THE HOs OF ETHANE

The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  of the C-C-bond MO are the same as those of the CH MO as well as each C-H-bond MO of the methyl groups except that energy of the  $C_{ethane} 2sp^3$  HO is used. The energies of each C-C-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.158-14.159) and (14.162)) into the energy equations of the CH MO (Eqs. (13.449-13.453)), with the exception that  $E(C_{ethane}, 2sp^3)$  replaces  $E(C, 2sp^3)$  in Eq. (13.453):

$$V_e = (0.91771) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -29.101124 \text{ eV} \tag{14.225}$$

$$V_p = \frac{e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 9.37273 \text{ eV} \tag{14.226}$$

$$T = (0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 6.90500 \text{ eV} \tag{14.227}$$

$$V_m = (0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -3.45250 \text{ eV} \quad (14.228)$$

$$E_T(C-C, \sigma) = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.35946 \text{ eV} = -31.63535 \text{ eV} \quad (14.229)$$

where  $E_T(C-C, \sigma)$  is the total energy of the  $C-C$   $\sigma$  MO given by Eq. (14.155) which is 5 reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

The total energy of the  $C-C$ -bond MO,  $E_T(C-C)$ , is given by the sum of two times  $E_T(C-C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell due to the decrease in radius with the formation of the  $C-C$ -bond MO (Eq. (14.151)), and  $E_T(C-C, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (14.156):

$$\begin{aligned} E_T(C-C) &= 2E_T(C-C, 2sp^3) + E_T(C-C, \sigma) \\ 10 \quad &= \left( 2(-0.72457 \text{ eV}) + \left( -\frac{e^2}{8\pi\epsilon_0 \sqrt{aa_0}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{aa_0}}{a - \sqrt{aa_0}} - 1 \right] - 15.35946 \text{ eV} \right) \right) \quad (14.230) \\ &= 2(-0.72457 \text{ eV}) + (-31.63537 \text{ eV}) \\ &= -33.08452 \text{ eV} \end{aligned}$$

## VIBRATION OF ETHANE

The vibrational energy levels of  $CH_3CH_3$  may be solved as two sets of three equivalent coupled harmonic oscillators with a bridging harmonic oscillator by developing the 15 Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $C-C$ -BOND MO OF ETHANE

20 The equations of the radiation reaction force of the symmetrical  $C-C$ -bond MO are given by Eqs. (11.231-11.233), except the force-constant factor is 0.5 based on the force constant  $k'$  of Eq. (14.152), and the  $C-C$ -bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is



$$\omega = \sqrt{\frac{0.5e^2}{4\pi\epsilon_0 a^3}} = 9.55643 \times 10^{15} \text{ rad/s} \quad (14.231)$$

where  $a$  is given by Eq. (14.158). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 9.55643 \times 10^{15} \text{ rad/s} = 6.29021 \text{ eV} \quad (14.232)$$

5 In Eq. (11.181), substitution of  $E_T(C-C)$  (Eq. (14.230)) for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (14.232) for  $\bar{E}_K$  gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -33.08450 \text{ eV} \sqrt{\frac{2e(6.29021 \text{ eV})}{m_e c^2}} = -0.16416 \text{ eV} \quad (14.233)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the  
10 transition state at their corresponding frequency. The decrease in the energy of the  $C-C$ -bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (14.233) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of the  $C-C$  bond. Using the experimental  
15  $C-C$   $E_{vib}(\nu_3)$  of  $993 \text{ cm}^{-1}$  ( $0.12312 \text{ eV}$ ) [10] for  $\bar{E}_{Kvib}$  of the transition state,  $\bar{E}_{osc}(C-C, \sigma)$  is

$$\bar{E}_{osc}(C-C, \sigma) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (14.234)$$

$$\bar{E}_{osc}(C-C, \sigma) = -0.16416 \text{ eV} + \frac{1}{2} (0.12312 \text{ eV}) = -0.10260 \text{ eV} \quad (14.235)$$

## 20 TOTAL ENERGIES OF THE $C-C$ -BOND MO OF ETHANE

$E_{T+osc}(C-C)$ , the total energy of the  $C-C$ -bond MO including the Doppler term, is given by the sum of  $E_T(C-C)$  (Eq. (14.230)) and  $\bar{E}_{osc}(C-C, \sigma)$  given by Eq. (14.235):

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$$\begin{aligned}
 E_{T+osc}(C-C) &= V_e + T + V_m + V_p + E(C_{ethane}, 2sp^3) + 2E_T(C-C, 2sp^3) + \bar{E}_{osc}(C-C, \sigma) \\
 &= E_T(C-C, \sigma) + 2E_T(C-C, 2sp^3) + \bar{E}_{osc}(C-C, \sigma) \\
 &= E_T(C-C) + \bar{E}_{osc}(C-C, \sigma)
 \end{aligned}
 \tag{14.236}$$

$$\begin{aligned}
 E_{T+osc}(C-C) &= \left\{ \left( \frac{-e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.35946 \text{ eV} + 2E_T(C-C, 2sp^3) \right) \right. \\
 &\quad \left. \left( 1 + \sqrt{\frac{2\hbar \sqrt{\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \right\} \\
 &= -33.08452 \text{ eV} - 0.16416 \text{ eV} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}
 \end{aligned}
 \tag{14.237}$$

5 From Eqs. (14.234-14.237), the total energy of the  $C-C$  -bond MO is

$$\begin{aligned}
 E_{T+osc}(C-C) &= -31.63537 \text{ eV} + 2E_T(C-C, 2sp^3) + \bar{E}_{osc}(C-C, \sigma) \\
 &= -31.63537 \text{ eV} + 2(-0.72457 \text{ eV}) - 0.16416 \text{ eV} + \frac{1}{2}(0.12312 \text{ eV}) \\
 &= -33.18712 \text{ eV}
 \end{aligned}
 \tag{14.238}$$

where the experimental  $E_{vib}$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

## BOND ENERGY OF THE $C-C$ BOND OF ETHANE

10 The dissociation energy of the  $C-C$  bond of  $CH_3CH_3$ ,  $E_D(H_3C-CH_3)$ , is given by two times  $E(C, 2sp^3)$  (Eq. (14.146)), the initial energy of the  $C2sp^3$  HO of each  $CH_3$  radical that bond with a single  $C-C$  bond, minus the sum of  $\Delta E_{T+osc}(^{12}CH_3)$  (Eq. (14.224)), the energy change going from the methyl radicals to the methyl groups of ethane, and  $E_{T+osc}(C-C)$  (Eq. (14.238)). Thus, the dissociation energy of the  $C-C$  bond of  $CH_3CH_3$ ,  
15 is

$$\begin{aligned}
 E_D(H_3C-CH_3) &= 2(E(C, 2sp^3)) - (\Delta E_{T+osc}(^{12}CH_3) + E_{T+osc}(C-C)) \\
 &= 2(-14.63489 \text{ eV}) - (0.01487 \text{ eV} - 33.18712 \text{ eV}) \\
 &= 2(-14.63489 \text{ eV}) - (33.17225 \text{ eV}) \\
 &= 3.90247 \text{ eV}
 \end{aligned}
 \tag{14.239}$$

The experimental dissociation energy of the  $C-C$  bond of  $CH_3CH_3$  is [6]

$$E_D(H_3C-CH_3) = 3.89690 \text{ eV} \quad (14.240)$$

The results of the determination of bond parameters of  $CH_3CH_3$  are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact 5 equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## ETHYLENE MOLECULE ( $CH_2CH_2$ )

The ethylene molecule  $CH_2CH_2$  is formed by the reaction of two dihydrogen carbide 10 radicals:



$CH_2CH_2$  can be solved using the same principles as those used to solve the methane series  $CH_{n=1,2,3,4}$ , wherein the  $2s$  and  $2p$  shells of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals 15 (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. First, two sets of two  $H$  atomic orbitals (AOs) combine with two sets of two carbon  $2sp^3$  HOs to form two dihydrogen carbide groups comprising a linear combination of four diatomic  $H_2$ -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. Then, the two  $CH_2$  groups bond by 20 forming a  $H_2$ -type MO between the remaining two  $C2sp^3$  HOs on each carbon atom.

## FORCE BALANCE OF THE $C=C$ -BOND MO OF ETHYLENE

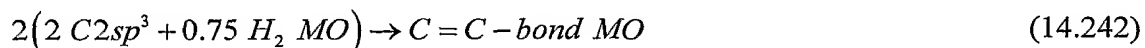
$CH_2CH_2$  comprises a chemical bond between two  $CH_2$  radicals wherein each radical comprises two chemical bonds between carbon and hydrogen atoms. The solution of the 25 parameters of  $CH_2$  is given in the Dihydrogen Carbide ( $CH_2$ ) section. Each  $C-H$  bond of  $CH_2$  having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75%  $H_2$ -type ellipsoidal MO and 25%  $C2sp^3$  HO. The proton of the  $H$  atom and the nucleus of the  $C$  atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , each of

the two  $C-H$ -bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the  $H$  proton that is continuous with the  $C2sp^3$  shell at the  $C$  atom whose nucleus serves as  
 5 the other focus. The electron configuration and the energy,  $E(C, 2sp^3)$ , of the  $C2sp^3$  shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of each  $C-H$  bond is provided by the spin-pairing force of the  $CH_2$  MO that has the symmetry of an  $s$  orbital that superimposes with the  $C2sp^3$  orbitals such that the corresponding angular momenta are unchanged.

10 Two  $CH_2$  radicals bond to form  $CH_2CH_2$  by forming a MO between the two pairs of remaining  $C2sp^3$ -HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between four  $C2sp^3$  HOs to form a molecular orbital (MO) comprising four spin-paired electrons permits each  $C2sp^3$  HO to decrease in radius and energy.

As in the case of the  $C-H$  bonds, the  $C=C$ -bond MO is a prolate-spheroidal-MO  
 15 surface that cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the  $C2sp^3$  shell at each  $C$  atom. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the  $C2sp^3$  shell. As in the case of previous examples of energy-matched MOs such as those of  $OH$ ,  $NH$ ,  $CH$ , the  $C=O$ -bond MO of  
 20  $CO_2$ , and the  $C-C$ -bond MO of  $CH_3CH_3$ , the  $C=C$ -bond MO of ethylene must comprise 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $C=C$ -bond MO must comprise a linear combination of two MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

25



The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution from each  $C2sp^3$  HO to the  $C=C$ -

bond MO to achieve an energy minimum. The force balance of the  $C = C$ -bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.242) and the energy matching condition between the  $C2sp^3$ -HO components of the MO.

5 Similarly, the energies of each  $CH_2$  MO involve each  $C2sp^3$  and each  $H1s$  electron with the formation of each  $C - H$  bond. The sum of the energies of the  $H_2$ -type ellipsoidal MOs is matched to that of the  $C2sp^3$  shell. This energy is determined by the considering the effect of the donation of 25% electron density from the two pairs of  $C2sp^3$  HOs to the  $C = C$ -bond MO with the formation of the  $C_{ethylene}2sp^3$  HOs each having a smaller radius.

10 The  $2sp^3$  hybridized orbital arrangement is given by Eq. (14.140). The sum  $E_T(C, 2sp^3)$  of calculated energies of  $C$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  is given by Eq. (14.141). The radius  $r_{2sp^3}$  of the  $C2sp^3$  shell is given by Eq. (14.142). The Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  and the energy  $E(C, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell are given by Eqs. (14.143) and (14.146), respectively.

15 Next, consider the formation of the  $C = C$ -bond MO of ethylene from two  $CH_2$  radicals, each having a  $C2sp^3$  electron with an energy given by Eq. (14.146). The total energy of the state is given by the sum over the four electrons. The sum  $E_T(C_{ethylene}, 2sp^3)$  of calculated energies of  $C2sp^3$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$\begin{aligned}
 E_T(C_{ethylene}, 2sp^3) &= -(64.3921 \text{ eV} + 48.3125 \text{ eV} + 24.2762 \text{ eV} + E(C, 2sp^3)) \\
 &= -(64.3921 \text{ eV} + 48.3125 \text{ eV} + 24.2762 \text{ eV} + 14.63489 \text{ eV}) \\
 &= -151.61569 \text{ eV}
 \end{aligned}$$

(14.243)

where  $E(C, 2sp^3)$  (Eq. (14.146)) is the sum of the energy of  $C$ ,  $-11.27671 \text{ eV}$ , and the hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the  $E_T(C_{ethylene}, 2sp^3)$  is purely Coulombic.

25 The sharing of electrons between two pairs of  $C2sp^3$  HOs to form a  $C = C$ -bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating

$C2sp^3$  HO donates an excess of 25% per bond of its electron density to the  $C = C$  -bond MO to form an energy minimum. By considering this electron redistribution in the ethylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{ethylene2sp^3}$  of the  $C2sp^3$  shell of ethylene may be calculated

5 from the Coulombic energy using Eq. (10.102):

$$r_{ethylene2sp^3} = \left( \sum_{n=2}^5 (Z - n) - 0.5 \right) \frac{e^2}{8\pi\epsilon_0 (e151.61569 \text{ eV})} = \frac{9.5e^2}{8\pi\epsilon_0 (e151.61569 \text{ eV})} = 0.85252a_0 \quad (14.244)$$

where  $Z = 6$  for carbon. Using Eqs. (10.102) and (14.244), the Coulombic energy  $E_{Coulomb}(C_{ethylene}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$10 \quad E_{Coulomb}(C_{ethylene}, 2sp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{ethylene2sp^3}} = \frac{-e^2}{8\pi\epsilon_0 0.85252a_0} = -15.95955 \text{ eV} \quad (14.245)$$

During hybridization, one of the spin-paired  $2s$  electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152). Using Eqs. (14.145) and (14.245), the energy  $E(C_{ethylene}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$\begin{aligned} E(C_{ethylene}, 2sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{ethylene2sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} \\ 15 \quad &= -15.95955 \text{ eV} + 0.19086 \text{ eV} \\ &= -15.76868 \text{ eV} \end{aligned} \quad (14.246)$$

Thus,  $E_T(C = C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell with the formation of the  $C = C$  -bond MO is given by the difference between Eq. (14.146) and Eq. (14.246):

$$\begin{aligned} E_T(C = C, 2sp^3) &= E(C_{ethylene}, 2sp^3) - E(C, 2sp^3) \\ &= -15.76868 \text{ eV} - (-14.63489 \text{ eV}) \\ &= -1.13380 \text{ eV} \end{aligned} \quad (14.247)$$

As in the case of  $Cl_2$ , each  $H_2$ -type ellipsoidal MO comprises 75% of the  $C = C$  -bond MO shared between two  $C2sp^3$  HOs corresponding to the electron charge density in Eq. (11.65) of  $\frac{-0.75e}{2}$ . But, the additional 25% charge-density contribution to each bond of the  $C = C$  -

bond MO causes the electron charge density in Eq. (11.65) to be is given by  $\frac{-e}{2} = -0.5e$ . The

corresponding force constant  $k'$  is given by Eq. (14.152). In addition, the energy matching at both  $C2sp^3$  HO further requires that  $k'$  be corrected by the hybridization factor given by Eq. (13.430). Thus, the force constant  $k'$  to determine the ellipsoidal parameter  $c'$  in terms of the central force of the foci (Eq. (11.65)) is given by

$$5 \quad k' = C_{C2sp^3 HO} \frac{(0.5)2e^2}{4\pi\epsilon_0} = 0.91771 \frac{(0.5)2e^2}{4\pi\epsilon_0} \quad (14.248)$$

The distance from the origin to each focus  $c'$  is given by substitution of Eq. (14.248) into Eq. (13.60). Thus, the distance from the origin of the component of the double  $C = C$ -bond MO to each focus  $c'$  is given by

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{(0.91771)m_e e^2 a}} = \sqrt{\frac{aa_0}{0.91771}} \quad (14.249)$$

10 The internuclear distance from Eq. (14.249) is

$$2c' = 2\sqrt{\frac{aa_0}{0.91771}} \quad (14.250)$$

The length of the semiminor axis of the prolate spheroidal  $C = C$ -bond MO  $b = c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of  
15 the  $C = C$ -bond MO. From the energy equation and the relationship between the axes, the dimensions of the  $C = C$ -bond MO are solved.

The general equations for the energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  of the  $C = C$ -bond MO are the same as those of the  $CH$  MO except that energy of the  $C_{ethylene}2sp^3$  HO is used and the double-bond nature is considered. In the case of a single bond, the prolate  
20 spheroidal  $H_2$ -type MO transitions to the  $C_{ethylene}2sp^3$  HO of each carbon, and the energy of the  $C_{ethylene}2sp^3$  shell must remain constant and equal to the  $E(C_{ethylene}, 2sp^3)$  given by Eq. (14.246). Thus, the energy  $E(C_{ethylene}, 2sp^3)$  in Eq. (14.246) adds to that of the energies of the corresponding  $H_2$ -type ellipsoidal MO. The second bond of the double  $C = C$ -bond MO also transitions to the  $C_{ethylene}2sp^3$  HO of each  $C$ . The energy of a second  $H_2$ -type  
25 ellipsoidal MO adds to the first energy component, and the two bonds achieve an energy minimum as a linear combination of the two  $H_2$ -type ellipsoidal MOs each having the carbon nuclei as the foci. Each  $C - C$ -bond MO comprises the same  $C_{ethylene}2sp^3$  HO shells of

constant energy given by Eq. (14.246). As in the case of the water,  $NH_2$ , and ammonia molecules given by Eqs. (13.180), (13.320), and (13.372), respectively, the energy of the redundant shell is subtracted from the total energy of the linear combination of the  $\sigma$  MO. Thus, the total energy  $E_T(C=C, \sigma)$  of the  $\sigma$  component of the  $C=C$ -bond MO is given by

5 the sum of the energies of the two bonds each comprising the linear combination of the  $C_{ethylene} 2sp^3$  HO and the  $H_2$ -type ellipsoidal MO as given by Eq. (14.242) wherein the  $E_T$  terms add positively, the  $E(C_{ethylene}, 2sp^3)$  terms cancel, and the energy matching condition between the components is provided by Eq. (14.248). Using Eqs. (13.431) and (14.246),  $E_T(C=C, \sigma)$  is given by

$$10 \quad E_T(C=C, \sigma) = E_T + E(C_{ethylene}, 2sp^3) - E(C_{ethylene}, 2sp^3) \\ = -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \quad (14.251)$$

The total energy term of the double  $C=C$ -bond MO is given by the sum of the two  $H_2$ -type ellipsoidal MOs given by Eq. (11.212). To match this boundary condition,  $E_T(C=C, \sigma)$  given by Eq. (14.251) is set equal to two times Eq. (13.75):

$$E_T(C=C, \sigma) = -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] = -63.27074 \text{ eV} \quad (14.252)$$

15 From the energy relationship given by Eq. (14.252) and the relationship between the axes given by Eqs. (14.249-14.250) and (13.62-13.63), the dimensions of the  $C=C$ -bond MO can be solved.

Substitution of Eq. (14.249) into Eq. (14.252) gives

$$\frac{2e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{0.91771}}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{0.91771}}}{a - \sqrt{\frac{aa_0}{0.91771}}} - 1 \right] = e63.27074 \quad (14.253)$$

20 The most convenient way to solve Eq. (14.253) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.47228a_0 = 7.79098 \times 10^{-11} \text{ m} \quad (14.254)$$

Substitution of Eq. (14.254) into Eq. (14.249) gives

$$c' = 1.26661a_0 = 6.70259 \times 10^{-11} \text{ m} \quad (14.255)$$

25 The internuclear distance given by multiplying Eq. (14.255) by two is



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$$2c' = 2.53321a_0 = 1.34052 \times 10^{-10} \text{ m} \quad (14.256)$$

The experimental bond distance is [3]

$$2c' = 1.339 \times 10^{-10} \text{ m} \quad (14.257)$$

Substitution of Eqs. (14.254-14.255) into Eq. (13.62) gives

$$b = c = 0.75055a_0 = 3.97173 \times 10^{-11} \text{ m} \quad (14.258)$$

Substitution of Eqs. (14.252-14.255) into Eq. (13.63) gives

$$e = 0.86030 \quad (14.259)$$

The nucleus of the  $C$  atoms comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{ethylene} 2sp^3$  HO

are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{ethylene 2sp^3} = 0.85252a_0$  is the radius of the  $C_{ethylene} 2sp^3$  shell.

Substitution of Eqs. (14.254-14.255) into Eq. (13.261) gives

$$\theta' = 129.84^\circ \quad (14.260)$$

Then, the angle  $\theta_{C=C_{ethylene} 2sp^3 HO}$  the radial vector of the  $C 2sp^3$  HO makes with the internuclear

axis is

$$\theta_{C=C_{ethylene} 2sp^3 HO} = 180^\circ - 129.84^\circ = 50.16^\circ \quad (14.261)$$

as shown in Figure 40.

Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C=C_{ethylene}, H_2 MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with each  $C_{ethylene} 2sp^3$  radial vector obeys the following relationship:

$$r_{ethylene 2sp^3} \sin \theta_{C=C_{ethylene} 2sp^3 HO} = 0.85252a_0 \sin \theta_{C=C_{ethylene} 2sp^3 HO} = b \sin \theta_{C=C_{ethylene}, H_2 MO} \quad (14.262)$$

such that

$$\theta_{C=C_{ethylene}, H_2 MO} = \sin^{-1} \frac{0.85252a_0 \sin \theta_{C=C_{ethylene} 2sp^3 HO}}{b} = \sin^{-1} \frac{0.85252a_0 \sin 50.16^\circ}{b} \quad (14.263)$$

with the use of Eq. (14.261). Substitution of Eq. (14.258) into Eq. (14.263) gives

$$\theta_{C=C_{ethylene}, H_2 MO} = 60.70^\circ \quad (14.264)$$

Then, the distance  $d_{C=C_{ethylene}, H_2 MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C=C_{ethylene}, H_2MO} = a \cos \theta_{C=C_{ethylene}, H_2MO} \quad (14.265)$$

Substitution of Eqs. (14.254) and (14.264) into Eq. (14.265) gives

$$d_{C=C_{ethylene}, H_2MO} = 0.72040a_0 = 3.81221 \times 10^{-11} \text{ m} \quad (14.266)$$

The distance  $d_{C=C_{ethylene} 2sp^3HO}$  along the internuclear axis from the origin of the  $C$  atom to the  
5 point of intersection of the orbitals is given by

$$d_{C=C_{ethylene} 2sp^3HO} = c' - d_{C=C_{ethylene}, H_2MO} \quad (14.267)$$

Substitution of Eqs. (14.255) and (14.266) into Eq. (14.267) gives

$$d_{C=C_{ethylene} 2sp^3HO} = 0.54620a_0 = 2.89038 \times 10^{-11} \text{ m} \quad (14.268)$$

## 10 FORCE BALANCE OF THE $CH_2$ MOs OF ETHYLENE

Each of the two equivalent  $CH_2$  MOs must comprise two  $C-H$  bonds with each comprising 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO as given by Eq. (13.494):

$$2[1 C2sp^3 + 0.75 H_2 MO] \rightarrow CH_2 MO \quad (14.269)$$

15

The force balance of the  $CH_2$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.494) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant  $k'$  to determine the ellipsoidal parameter  $c'$  of the each  $H_2$ -type-  
20 ellipsoidal-MO component of the  $CH_2$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each  $C-H$ -bond MO to each focus  $c'$  is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal  $C-H$ -bond MO  $b = c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for  
25 the solution of the other axes of each prolate spheroid and eccentricity of each  $C-H$ -bond MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH_2$  MO are solved.

Consider the formation of the double  $C=C$ -bond MO of ethylene from two  $CH_2$  radicals, each having a  $C2sp^3$  shell with an energy given by Eq. (14.146). The energy

components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  are the same as those of the dihydrogen carbide radical, two times those of  $CH$  corresponding to the two  $C-H$  bonds, except that two times  $E_T(C=C, 2sp^3)$  is subtracted from  $E_T(CH_2)$  of Eq. (13.495). The subtraction of the energy change of the  $C2sp^3$  shells with the formation of the  $C=C$ -bond MO matches the energy of  
 5 the  $C-H$ -bond MOs to the decrease in the energy of the  $C2sp^3$  HOs. Using Eqs. (13.495) and (14.247),  $E_{T_{ethylene}}(CH_2)$  is given by

$$E_{T_{ethylene}}(CH_2) = E_T + E(C, 2sp^3) - 2E_T(C=C, 2sp^3) \\ = \left( -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \right. \\ \left. -14.63489 \text{ eV} - (-2.26758 \text{ eV}) \right) \quad (14.270)$$

$E_{T_{ethylene}}(CH_2)$  given by Eq. (14.270) is set equal to two times the energy of the  $H_2$ -type ellipsoidal MO minus the Coulombic energy of  $H$  given by Eq. (13.496):

$$10 \quad E_{T_{ethylene}}(CH_2) = \left( -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \right. \\ \left. -14.63489 \text{ eV} - (-2.26758 \text{ eV}) \right) = -49.66493 \text{ eV} \\ (14.271)$$

From the energy relationship given by Eq. (14.271) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH_2$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.271) gives

$$15 \quad \frac{2e^2}{8\pi\epsilon_0 \sqrt{\frac{2aa_0}{3}}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right] = e37.29762 \quad (14.272)$$

The most convenient way to solve Eq. (14.272) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.56946a_0 = 8.30521 \times 10^{-11} \text{ m} \quad (14.273)$$

Substitution of Eq. (14.273) into Eq. (13.60) gives

$$20 \quad c' = 1.02289a_0 = 5.41290 \times 10^{-11} \text{ m} \quad (14.274)$$

The internuclear distance given by multiplying Eq. (14.274) by two is

$$2c' = 2.04578a_0 = 1.08258 \times 10^{-10} \text{ m} \quad (14.275)$$

The experimental bond distance is [3]

$$2c' = 1.087 \times 10^{-10} \text{ m} \quad (14.276)$$

Substitution of Eqs. (14.273-14.274) into Eq. (14.62) gives

$$b = c = 1.19033a_0 = 6.29897 \times 10^{-11} \text{ m} \quad (14.277)$$

Substitution of Eqs. (14.273-14.274) into Eq. (14.63) gives

$$5 \quad e = 0.65175 \quad (14.278)$$

The nucleus of the  $H$  atom and the nucleus of the  $C$  atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{ethylene} 2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270).

The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{ethylene 2sp^3} = 0.85252a_0$  is

10 the radius of the  $C_{ethylene} 2sp^3$  shell. Substitution of Eqs. (14.273-14.274) into Eq. (13.261) gives

$$\theta' = 84.81^\circ \quad (14.279)$$

Then, the angle  $\theta_{C-H_{ethylene} 2sp^3 HO}$  the radial vector of the  $C 2sp^3$  HO makes with the internuclear axis is

$$15 \quad \theta_{C-H_{ethylene} 2sp^3 HO} = 180^\circ - 84.81^\circ = 95.19^\circ \quad (14.280)$$

as shown in Figure 41.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-H_{ethylene}, H_2 MO}$  between the

20 internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{ethylene} 2sp^3$  radial vector obeys the following relationship:

$$r_{ethylene 2sp^3} \sin \theta_{C-H_{ethylene} 2sp^3 HO} = 0.85252a_0 \sin \theta_{C-H_{ethylene} 2sp^3 HO} = b \sin \theta_{C-H, H_2 MO} \quad (14.281)$$

such that

$$\theta_{C-H_{ethylene}, H_2 MO} = \sin^{-1} \frac{0.85252a_0 \sin \theta_{C-H_{ethylene} 2sp^3 HO}}{b} = \sin^{-1} \frac{0.85252a_0 \sin 95.19^\circ}{b} \quad (14.282)$$

25 with the use of Eq. (14.280). Substitution of Eq. (14.277) into Eq. (14.282) gives

$$\theta_{C-H_{ethylene}, H_2 MO} = 45.50^\circ \quad (14.283)$$

Then, the distance  $d_{C-H_{ethylene}, H_2 MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{ethylene}, H_2MO} = a \cos \theta_{C-H_{ethylene}, H_2MO} \quad (14.284)$$

Substitution of Eqs. (14.273) and (14.283) into Eq. (14.284) gives

$$d_{C-H_{ethylene}, H_2MO} = 1.10002a_0 = 5.82107 \times 10^{-11} \text{ m} \quad (14.285)$$

The distance  $d_{C-H_{ethylene} 2sp^3 HO}$  along the internuclear axis from the origin of the  $C$  atom to the  
5 point of intersection of the orbitals is given by

$$d_{C-H_{ethylene} 2sp^3 HO} = d_{C-H_{ethylene}, H_2MO} - c' \quad (14.286)$$

Substitution of Eqs. (14.274) and (14.285) into Eq. (14.286) gives

$$d_{C-H_{ethylene} 2sp^3 HO} = 0.07713a_0 = 4.08171 \times 10^{-12} \text{ m} \quad (14.287)$$

## 10 BOND ANGLE OF THE $CH_2$ GROUPS

Each  $CH_2$  MO comprises a linear combination of two  $C-H$ -bond MOs. Each  $C-H$ -bond MO comprises the superposition of a  $H_2$ -type ellipsoidal MO and the  $C_{ethylene} 2sp^3$  HO. A bond is also possible between the two H atoms of the  $C-H$  bonds. Such  $H-H$  bonding would decrease the  $C-H$  bond strength since electron density would be shifted from the  
15  $C-H$  bonds to the  $H-H$  bond. Thus, the bond angle between the two  $C-H$  bonds is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal  $H$  atoms of the  $C-H$  bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the  $H-H$  ellipsoidal MO is

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \quad (14.288)$$

20 The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \quad (14.289)$$

The length of the semiminor axis of the prolate spheroidal  $H-H$  MO  $b = c$  is given by Eq. (14.62).

The bond angle of the  $CH_2$  groups of ethane is derived by using the orbital  
25 composition and an energy matching factor as in the case with the dihydrogen carbide radical and the  $CH_3$  groups of ethane. Since the two  $H_2$ -type ellipsoidal MOs initially comprise 75% of the  $H$  electron density of  $H_2$  and the energy of each  $H_2$ -type ellipsoidal MO is matched to that of the  $C_{ethylene} 2sp^3$  HO, the component energies and the total energy  $E_T$  of the

$H-H$  bond are given by Eqs. (13.67-13.73) except that  $V_e$ ,  $T$ , and  $V_m$  are corrected for the hybridization-energy-matching factor of 0.85252. Hybridization with 25% electron donation to the  $C=C$ -bond gives rise to the  $C_{ethylene} 2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(C_{ethylene}, 2sp^3)$  given by Eq. (14.245). The corresponding normalization factor for determining the zero of the total  $H-H$  bond energy is given by the ratio of 15.95955 eV, the magnitude of  $E_{Coulomb}(C_{ethylene}, 2sp^3)$  given by Eq. (14.245), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). The hybridization energy factor  $C_{ethyleneC2sp^3HO}$  is

$$C_{ethyleneC2sp^3HO} = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{ethylene2sp^3}}} = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 0.85252 a_0}} = \frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252 \quad (14.290)$$

Substitution of Eq. (14.290) into Eq. (13.233) or Eq. (14.195) with the hybridization factor of 0.85252 gives

$$0 = \left[ \frac{-e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2}}} \left[ (0.85252)^{-1} \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 a^3}}}}{m_e c^2} \right] \right. \\ \left. + \hbar \sqrt{\frac{\frac{0.75e^2}{8\pi\epsilon_0 a^3} - \frac{e^2}{8\pi\epsilon_0 (a+c')^3}}{0.5m_p}} \right] \quad (14.291)$$

From the energy relationship given by Eq. (14.291) and the relationship between the axes given by Eqs. (14.192-14.193) and (14.62-14.63), the dimensions of the  $H-H$  MO can be solved.

The most convenient way to solve Eq. (14.291) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 6.0400a_0 = 3.1962 \times 10^{-10} \text{ m} \quad (14.292)$$

Substitution of Eq. (14.292) into Eq. (14.288) gives

$$c' = 1.7378a_0 = 9.1961 \times 10^{-11} \text{ m} \quad (14.293)$$

The internuclear distance given by multiplying Eq. (14.293) by two is

$$2c' = 3.4756a_0 = 1.8392 \times 10^{-10} \text{ m} \quad (14.294)$$

Substitution of Eqs. (14.292-14.293) into Eq. (14.62) gives

$$b = c = 5.7846a_0 = 3.0611 \times 10^{-10} \text{ m} \quad (14.295)$$

Substitution of Eqs. (14.292-14.293) into Eq. (14.63) gives

$$e = 0.2877 \quad (14.296)$$

From,  $2c'_{H-H}$  (Eq. (14.294)), the distance between the two  $H$  atoms when the total energy of the corresponding MO is zero (Eq. (14.291)), and  $2c'_{C-H}$  (Eq. (14.275)), the internuclear distance of each  $C-H$  bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle  $\theta_{HCH}$  between the  $C-H$  bonds

10 is

$$\theta_{HCH} = \cos^{-1} \left( \frac{2(2.04578)^2 - (3.4756)^2}{2(2.04578)^2} \right) = \cos^{-1}(-0.44318) = 116.31^\circ \quad (14.297)$$

The experimental angle between the  $C-H$  bonds is [11]

$$\theta_{HCH} = 116.6^\circ \quad (14.298)$$

The  $C=C$  bond is along the  $z$ -axis. Thus, based on the symmetry of the equivalent bonds,  
15 the bond angle  $\theta_{C=C-H}$  between the internuclear axis of the  $C=C$  bond and a  $H$  atom of the  $CH_2$  groups is given by

$$\theta_{C=C-H} = \frac{(360^\circ - \theta_{CHC})}{2} \quad (14.299)$$

Substitution of Eq. (14.298) into Eq. (14.299) gives

$$\theta_{C=C-H} = 121.85^\circ \quad (14.300)$$

20 The experimental angle between the  $C=C-H$  bonds is [11]

$$\theta_{C=C-H} = 121.7^\circ \quad (14.301)$$

and [3]

$$\theta_{C=C-H} = 121.3^\circ \quad (14.302)$$

The  $C=C$  bond and  $H$  atoms of ethylene line in a plane, and rotation about the  $C=C$  is  
25 not possible due to conservation of angular momentum in the two sets of spin-paired electrons of the double bond. The  $CH_2CH_2$  MO shown in Figure 42 was rendered using these parameters.

The charge-density in the  $C=C$ -bond MO is increased by a factor of 0.25 per bond with the formation of the  $C_{ethylene} 2sp^3$  HOs each having a smaller radius. Using the orbital

composition of the  $CH_2$  groups (Eq. (14.269)) and the  $C=C$ -bond MO (Eq. (14.242), the radii of  $Cl_s = 0.17113a_0$  (Eq. (10.51)) and  $C_{ethylene} 2sp^3 = 0.85252a_0$  (Eq. (14.244)) shells, and the parameters of the  $C=C$ -bond (Eqs. (13.3-13.4), (14.254-14.256), and (14.258-14.268)), the parameters of the  $C-H$ -bond MOs (Eqs. (13.3-13.4), (14.273-14.275), and (14.277-14.287)), and the bond-angle parameters (Eqs. (14.297-14.302)), the charge-density of the  $CH_2CH_2$  MO comprising the linear combination of two sets of two  $C-H$ -bond MOs and a  $C=C$ -bond MO bridging the two  $CH_2$  groups is shown in Figure 42. Each  $C-H$ -bond MO comprises a  $H_2$ -type ellipsoidal MO and a  $C_{ethylene} 2sp^3$  HO having the dimensional diagram shown in Figure 41. The  $C=C$ -bond MO comprises a  $H_2$ -type ellipsoidal MO  
 10 bridging two  $C_{ethylene} 2sp^3$  HOs having the dimensional diagram shown in Figure 40.

### ENERGIES OF THE $CH_2$ GROUPS

The energies of each  $CH_2$  group of ethylene are given by the substitution of the semiprincipal axes (Eqs. (14.273-14.274) and (14.277)) into the energy equations of dihydrogen carbide  
 15 (Eqs. (13.510-13.514)), with the exception that two times  $E_T(C=C, 2sp^3)$  (Eq. (14.247)) is subtracted from  $E_T(CH_2)$  in Eq. (13.514):

$$V_e = 2(0.91771) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -76.00757 \text{ eV} \quad (14.303)$$

$$V_p = \frac{2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 26.60266 \text{ eV} \quad (14.304)$$

$$T = 2(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 24.21459 \text{ eV} \quad (14.305)$$

$$20 \quad V_m = 2(0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -12.10730 \text{ eV} \quad (14.306)$$

$$E_{T_{ethylene}}(CH_2) = \left( \frac{-2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \right. \\ \left. -14.63489 \text{ eV} - (-2.26758 \text{ eV}) \right) = -49.66493 \text{ eV} \quad (14.307)$$



where  $E_{\sigma_{ethylene}}(CH_2)$  is given by Eq. (14.270) which is reiteratively matched to Eq. (13.496) within five-significant-figure round off error.

## VIBRATION OF THE $^{12}CH_2$ GROUPS

5 The vibrational energy levels of  $CH_2$  in ethylene may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

10

## THE DOPPLER ENERGY TERMS OF THE $^{12}CH_2$ GROUPS

The equations of the radiation reaction force of the  $CH_2$  groups in ethylene are the same as those of the dihydrogen carbide radical with the substitution of the  $CH_2$ -group parameters. Using Eq. (13.515), the angular frequency of the reentrant oscillation in the transition state is

$$15 \quad \omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 2.75685 \times 10^{16} \text{ rad/s} \quad (14.308)$$

where  $b$  is given by Eq. (14.277). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.75685 \times 10^{16} \text{ rad/s} = 18.14605 \text{ eV} \quad (14.309)$$

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total  
20 energy of each  $H_2$ -type MO, for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (14.309) for  $\bar{E}_K$  gives the Doppler energy of the electrons of each of the two bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(18.14605 \text{ eV})}{m_e c^2}} = -0.26660 \text{ eV} \quad (14.310)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the  
25 transition state at their corresponding frequency. The decrease in the energy of  $CH_2$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding

energies,  $\bar{E}_D$  given by Eq. (14.310) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of each  $C-H$  bond. Using  $\omega_e$  given by Eq. (13.458) for  $\bar{E}_{Kvib}$  of the transition state having two independent bonds,  $\bar{E}'_{ethylene\ osc} (^{12}CH_2)$  per bond is

$$\bar{E}'_{ethylene\ osc} (^{12}CH_2) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (14.311)$$

$$5 \quad \bar{E}'_{ethylene\ osc} (^{12}CH_2) = -0.26660 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) = -0.08894 \text{ eV} \quad (14.312)$$

Given that the vibration and reentrant oscillation is for two  $C-H$  bonds,  $\bar{E}_{ethylene\ osc} (^{12}CH_2)$ , is:

$$\begin{aligned} \bar{E}_{ethylene\ osc} (^{12}CH_2) &= 2 \left( \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \\ &= 2 \left( -0.26660 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) \right) \\ &= -0.17788 \text{ eV} \end{aligned} \quad (14.313)$$

## 10 TOTAL AND DIFFERENCE ENERGIES OF THE $^{12}CH_2$ GROUPS

$E_{ethyleneT+osc} (^{12}CH_2)$ , the total energy of each  $^{12}CH_2$  group including the Doppler term, is given by the sum of  $E_{T_{ethylene}} (CH_2)$  (Eq. (14.307)) and  $\bar{E}_{ethylene\ osc} (^{12}CH_2)$  given by Eq. (14.313):

$$\begin{aligned} E_{ethyleneT+osc} (CH_2) &= \left( V_e + T + V_m + V_p + E(C, 2sp^3) \right. \\ &\quad \left. - 2E_T (C = C, 2sp^3) + \bar{E}_{ethylene\ osc} (^{12}CH_2) \right) \\ &= E_{T_{ethylene}} (CH_2) + \bar{E}_{ethylene\ osc} (^{12}CH_2) \end{aligned} \quad (14.314)$$

$$\begin{aligned} E_{ethyleneT+osc} (^{12}CH_2) &= \left\{ \begin{aligned} &\left( \frac{-2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \right) \\ &-14.63489 \text{ eV} - (-2.26759 \text{ eV}) \end{aligned} \right\} \\ &\quad \left\{ \begin{aligned} &-2 \left( (31.63536831 \text{ eV}) \sqrt{\frac{2\hbar \sqrt{\frac{3}{4} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}} \right) \end{aligned} \right\} \\ &= -49.66493 \text{ eV} - 2 \left( 0.26660 \text{ eV} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \end{aligned} \quad (14.315)$$

From Eqs. (14.313-14.315), the total energy of each  $^{12}\text{CH}_2$  is

$$\begin{aligned} E_{\text{ethylene}T+\text{osc}}(^{12}\text{CH}_2) &= -49.66493 \text{ eV} + \bar{E}_{\text{ethylene osc}}(^{12}\text{CH}_2) \\ &= -49.66493 \text{ eV} - 2 \left( 0.26660 \text{ eV} - \frac{1}{2} (0.35532 \text{ eV}) \right) \\ &= -49.84282 \text{ eV} \end{aligned} \quad (14.316)$$

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

The total energy for each dihydrogen carbide radical given by Eq. (13.523) is

$$\begin{aligned} E_{\text{radical}T+\text{osc}}(^{12}\text{CH}_2) &= -49.66493 \text{ eV} + \bar{E}_{\text{radical osc}}(^{12}\text{CH}_2) \\ &= -49.66493 \text{ eV} - 2 \left( 0.25493 \text{ eV} - \frac{1}{2} (0.35532 \text{ eV}) \right) \\ &= -49.81948 \text{ eV} \end{aligned} \quad (14.317)$$

The difference in energy between the  $\text{CH}_2$  groups and the dihydrogen carbide radical

$\Delta E_{T+\text{osc}}(^{12}\text{CH}_2)$  is given by two times the difference between Eqs. (14.316) and (14.317):

$$\begin{aligned} \Delta E_{T+\text{osc}}(^{12}\text{CH}_2) &= 2 \left( E_{\text{ethylene}T+\text{osc}}(^{12}\text{CH}_2) - E_{\text{radical}T+\text{osc}}(^{12}\text{CH}_2) \right) \\ &= 2 \left( -49.84282 \text{ eV} - (-49.81948 \text{ eV}) \right) \\ &= -0.04667 \text{ eV} \end{aligned} \quad (14.318)$$

## 10 SUM OF THE ENERGIES OF THE $\text{C}=\text{C}$ $\sigma$ MO AND THE HOs OF ETHYLENE

The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  of the  $\text{C}=\text{C}$ -bond MO are the same as those of the  $\text{CH}$  MO except that each term is multiplied by two corresponding to the double bond and the energy term corresponding to the  $C_{\text{ethylene}} 2sp^3$  HOs in the equation for  $E_T$  is zero. The energies of each  $\text{C}=\text{C}$ -bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.254-14.255) and (14.258)) into two times the energy equations of the  $\text{CH}$  MO (Eqs. (13.449-13.453)), with the exception that zero replaces  $E(\text{C}, 2sp^3)$  in Eq. (13.453):

$$V_e = 2(0.91771) \frac{-2e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -102.08992 \text{ eV} \quad (14.319)$$

$$V_p = 2 \frac{e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} = 21.48386 \text{ eV} \quad (14.320)$$

$$T = 2(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 34.67062 \text{ eV} \quad (14.321)$$

$$V_m = 2(0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -17.33531 \text{ eV} \quad (14.322)$$

$$E_T(C = C, \sigma) = -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] = -63.27075 \text{ eV} \quad (14.323)$$

where  $E_T(C = C, \sigma)$  is the total energy of the  $C = C$   $\sigma$  MO given by Eq. (14.251) which is reiteratively matched to two times Eq. (13.75) within five-significant-figure round off error.

The total energy of the  $C = C$  -bond MO,  $E_T(C = C)$ , is given by the sum of two times  $E_T(C = C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell due to the decrease in radius with the formation of the  $C = C$  -bond MO (Eq. (14.247)), and  $E_T(C = C, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (14.252):

$$\begin{aligned} E_T(C = C) &= 2E_T(C = C, 2sp^3) + E_T(C = C, \sigma) \\ &= \left( 2(-1.13380 \text{ eV}) + \left( -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \right) \right) \\ &= 2(-1.13380 \text{ eV}) + (-63.27074 \text{ eV}) \\ &= -65.53833 \text{ eV} \end{aligned} \quad (14.324)$$

## VIBRATION OF ETHYLENE

The vibrational energy levels of  $CH_2CH_2$  may be solved as two sets of two equivalent coupled harmonic oscillators with a bridging harmonic oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $C = C$ -BOND MO OF ETHYLENE

The equations of the radiation reaction force of the  $C = C$  -bond MO are given by Eq. (13.142), except the force-constant factor is  $(0.93172)0.5$  based on the force constant  $k'$  of

Eq. (14.248), and the  $C = C$  -bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.91771 \frac{(0.5)e^2}{4\pi\epsilon_0 b^3}}{m_e}} = 4.30680 \times 10^{16} \text{ rad/s} \quad (14.325)$$

where  $b$  is given by Eq. (14.258). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. 5 (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 4.30680 \times 10^{16} \text{ rad/s} = 28.34813 \text{ eV} \quad (14.326)$$

In Eq. (11.181), substitution of  $E_T(C = C)/2$  (Eq. (14.324)) for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (14.326) for  $\bar{E}_K$  gives the Doppler energy of the electrons of each of the two bonds for the reentrant orbit:

$$10 \quad \bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -32.76916 \text{ eV} \sqrt{\frac{2e(28.34813 \text{ eV})}{m_e c^2}} = -0.34517 \text{ eV} \quad (14.327)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the  $C = C$  -bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the 15 corresponding energies,  $\bar{E}_D$  given by Eq. (14.327) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of the  $C = C$  bond. Using the experimental  $C = C$   $E_{vib}(\nu_3)$  of  $1443.5 \text{ cm}^{-1}$  ( $0.17897 \text{ eV}$ ) [12] for  $\bar{E}_{Kvib}$  of the transition state having two bonds,  $\bar{E}'_{osc}(C = C, \sigma)$  per bond is

$$\bar{E}'_{osc}(C = C, \sigma) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (14.328)$$

$$20 \quad \bar{E}'_{osc}(C = C, \sigma) = -0.34517 \text{ eV} + \frac{1}{2} (0.17897 \text{ eV}) = -0.25568 \text{ eV} \quad (14.329)$$

Given that the vibration and reentrant oscillation is for two  $C - C$  bonds of the  $C = C$  double bond,  $\bar{E}_{ethylene\ osc}(C = C, \sigma)$ , is:

$$\bar{E}_{ethylene\ osc}(C = C, \sigma) = 2 \left( \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) = 2 \left( -0.34517 \text{ eV} + \frac{1}{2} (0.17897 \text{ eV}) \right) = -0.51136 \text{ eV} \quad (14.330)$$

TOTAL ENERGIES OF THE  $C=C$  -BOND MO OF ETHYLENE

$E_{T+osc}(C=C)$ , the total energy of the  $C=C$  -bond MO including the Doppler term, is given by the sum of  $E_T(C=C)$  (Eq. (14.324)) and  $\bar{E}_{ethylene\ osc}(C=C, \sigma)$  given by Eq. (14.330):

$$\begin{aligned} E_{T+osc}(C=C) &= V_e + T + V_m + V_p + 2E_T(C=C, 2sp^3) + \bar{E}_{ethylene\ osc}(C=C, \sigma) \\ &= E_T(C=C, \sigma) + 2E_T(C=C, 2sp^3) + \bar{E}_{ethylene\ osc}(C=C, \sigma) \\ &= E_T(C=C) + \bar{E}_{ethylene\ osc}(C=C, \sigma) \end{aligned} \quad (14.331)$$

$$\begin{aligned} E_{T+osc}(C=C) &= \left\{ \left( \frac{-2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] + 2E_T(C=C, 2sp^3) \right) \right. \\ &\quad \left. \left( 1 + (2) \left( \frac{1}{2} \right) \sqrt{\frac{2\hbar \sqrt{(0.91771) \frac{1}{2} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2}} + 2 \left( \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \right) \right\} \\ &= -65.53833 \text{ eV} - 2 \left( 0.34517 \text{ eV} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \end{aligned} \quad (14.332)$$

From Eqs. (14.330-14.332), the total energy of the  $C=C$  -bond MO is

$$\begin{aligned} E_{T+osc}(C=C) &= -63.27074 \text{ eV} + 2E_T(C=C, 2sp^3) + \bar{E}_{ethylene\ osc}(C=C, \sigma) \\ &= -63.27074 \text{ eV} + 2(-1.13380 \text{ eV}) - 2 \left( 0.34517 \text{ eV} - \frac{1}{2} (0.17897 \text{ eV}) \right) \\ &= -66.04969 \text{ eV} \end{aligned} \quad (14.333)$$

where the experimental  $E_{vib}$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

10

BOND ENERGY OF THE  $C=C$  BOND OF ETHYLENE

The dissociation energy of the  $C=C$  bond of  $CH_2CH_2$ ,  $E_D(H_2C=CH_2)$ , is given by four times  $E(C, 2sp^3)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each  $CH_2$  radical that forms the double  $C=C$  bond, minus the sum of  $\Delta E_{T+osc}(^{12}CH_2)$  (Eq. (14.318)), the energy change going from the dihydrogen carbide radicals to the  $CH_2$  groups of ethylene, and  $E_{T+osc}(C=C)$  (Eq. (14.333)). Thus, the dissociation energy of the  $C=C$  bond of  $CH_2CH_2$ , is

$$\begin{aligned}
 E_D(H_2C=CH_2) &= 4 \left( E(C, 2sp^3) \right) - \left( \Delta E_{T+osc}({}^{12}CH_2) + E_{T+osc}(C=C) \right) \\
 &= 4(-14.63489 \text{ eV}) - (-0.04667 \text{ eV} - 66.04969 \text{ eV}) \\
 &= 4(-14.63489 \text{ eV}) - (-66.09636 \text{ eV}) \\
 &= 7.55681 \text{ eV}
 \end{aligned}
 \tag{14.334}$$

The experimental dissociation energy of the  $C=C$  bond of  $CH_2CH_2$  is [7]

$$E_D(H_2C-CH_2) = 7.5969 \text{ eV} \tag{14.335}$$

The results of the determination of bond parameters of  $CH_2CH_2$  are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

### ACETYLENE MOLECULE ( $CHCH$ )

10 The acetylene molecule  $CHCH$  is formed by the reaction of two hydrogen carbide radicals:



$CHCH$  can be solved using the same principles as those used to solve the methane series  $CH_{n=1,2,3,4}$  as well as ethane, wherein the  $2s$  and  $2p$  shells of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. First, two sets of one  $H$  atomic orbital (AO) combine with two sets of one carbon  $2sp^3$  HO to form two hydrogen carbide groups comprising a linear combination of two diatomic  $H_2$ -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. Then, the two  $CH$  groups bond by forming a  $H_2$ -type MO between the remaining three  $C2sp^3$  HOs on each carbon atom.

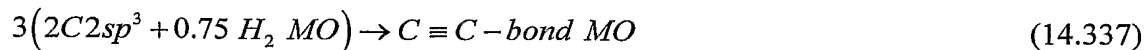
### FORCE BALANCE OF THE $C \equiv C$ -BOND MO OF ACETYLENE

$CHCH$  comprises a chemical bond between two  $CH$  radicals wherein each radical comprises a chemical bond between a carbon and a hydrogen atom. The solution of the parameters of  $CH$  is given in the Hydrogen Carbide ( $CH$ ) section. The  $C-H$  bond of  $CH$  having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75%  $H_2$ -type

ellipsoidal MO and 25%  $C2sp^3$  HO. The proton of the  $H$  atom and the nucleus of the  $C$  atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , the  $C-H$ -bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, the MO surface comprises a prolate spheroid at the  $H$  proton that is continuous with the  $C2sp^3$  shell at the  $C$  atom whose nucleus serves as the other focus. The electron configuration and the energy,  $E(C, 2sp^3)$ , of the  $C2sp^3$  shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of the  $C-H$  bond is provided by the spin-pairing force of the  $CH$  MO that has the symmetry of an  $s$  orbital that superimposes with the  $C2sp^3$  orbitals such that the corresponding angular momenta are unchanged.

Two  $CH$  radicals bond to form  $CHCH$  by forming a MO between the two pairs of three remaining  $C2sp^3$ -HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between two  $C2sp^3$  HOs to form a MO comprising six spin-paired electrons permits each  $C2sp^3$  HO to decrease in radius and energy.

As in the case of the  $C-H$  bonds, the  $C \equiv C$ -bond MO is a prolate-spheroidal-MO surface that cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the  $C2sp^3$  shell at each  $C$  atom. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the  $C2sp^3$  shell. As in the case of previous examples of energy-matched MOs such as those of  $OH$ ,  $NH$ ,  $CH$ , the  $C=O$ -bond MO of  $CO_2$ , the  $C-C$ -bond MO of  $CH_3CH_3$ , and the  $C=C$ -bond MO of  $CH_2CH_2$ , the  $C \equiv C$ -bond MO of acetylene must comprise 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $C \equiv C$ -bond MO must comprise a linear combination of three MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:





The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution from each  $C2sp^3$  HO to the  $C \equiv C$ -bond MO to achieve an energy minimum. The force balance of the  $C \equiv C$ -bond MO is determined by the boundary conditions that arise from the linear combination of orbitals  
 5 according to Eq. (14.337) and the energy matching condition between the  $C2sp^3$ -HO components of the MO.

Similarly, the energies of each  $CH$  MO involve each  $C2sp^3$  and each  $H1s$  electron with the formation of each  $C-H$  bond. The sum of the energies of the  $H_2$ -type ellipsoidal MOs is matched to that of the  $C2sp^3$  shell. This energy is determined by the considering the  
 10 effect of the donation of 25% electron density from the three pairs of  $C2sp^3$  HOs to the  $C \equiv C$ -bond MO with the formation of the  $C_{acetylene}2sp^3$  HOs each having a smaller radius. The  $2sp^3$  hybridized orbital arrangement is given by Eq. (14.140). The sum  $E_T(C, 2sp^3)$  of calculated energies of  $C$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  is given by Eq. (14.141). The radius  $r_{2sp^3}$  of the  $C2sp^3$  shell is given by Eq. (14.142). The Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  and the  
 15 energy  $E(C, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell are given by Eqs. (14.143) and (14.146), respectively.

Next, consider the formation of the  $C \equiv C$ -bond MO of acetylene from two  $CH$  radicals, each having a  $C2sp^3$  electron with an energy given by Eq. (14.146). The total energy of the state is given by the sum over the four electrons. The sum  $E_T(C_{acetylene}, 2sp^3)$  of  
 20 calculated energies of  $C2sp^3$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$\begin{aligned} E_T(C_{acetylene}, 2sp^3) &= -(64.3921 \text{ eV} + 48.3125 \text{ eV} + 24.2762 \text{ eV} + E(C, 2sp^3)) \\ &= -(64.3921 \text{ eV} + 48.3125 \text{ eV} + 24.2762 \text{ eV} + 14.63489 \text{ eV}) \\ &= -151.61569 \text{ eV} \end{aligned}$$

(14.338)

where  $E(C, 2sp^3)$  (Eq. (14.146)) is the sum of the energy of  $C$ ,  $-11.27671 \text{ eV}$ , and the  
 25 hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the  $E_T(C_{acetylene}, 2sp^3)$  is purely Coulombic.

The sharing of electrons between three pairs of  $C2sp^3$  HOs to form a  $C \equiv C$  -bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating  $C2sp^3$  HO donates an excess of 25% of its electron density to the  $C \equiv C$  -bond MO to form an energy minimum. By considering this electron redistribution in the acetylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{acetylene2sp^3}$  of the  $C2sp^3$  shell of acetylene may be calculated from the Coulombic energy using Eq. (10.102):

$$\begin{aligned} r_{acetylene2sp^3} &= \left( \sum_{n=2}^5 (Z - n) - 0.75 \right) \frac{e^2}{8\pi\epsilon_0 (e151.61569 \text{ eV})} \\ &= \frac{9.25e^2}{8\pi\epsilon_0 (e151.61569 \text{ eV})} \\ &= 0.83008a_0 \end{aligned} \quad (14.339)$$

where  $Z = 6$  for carbon. Using Eqs. (10.102) and (14.339), the Coulombic energy  $E_{Coulomb}(C_{acetylene}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E_{Coulomb}(C_{acetylene}, 2sp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{acetylene2sp^3}} = \frac{-e^2}{8\pi\epsilon_0 0.83008a_0} = -16.39089 \text{ eV} \quad (14.340)$$

During hybridization, one of the spin-paired  $2s$  electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152). Using Eqs. (14.145) and (14.340), the energy  $E(C_{acetylene}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$\begin{aligned} E(C_{acetylene}, 2sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{acetylene2sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} = -16.39089 \text{ eV} + 0.19086 \text{ eV} = -16.20002 \text{ eV} \\ & \quad (14.341) \end{aligned}$$

Thus,  $E_T(C \equiv C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell with the formation of the  $C \equiv C$  -bond MO is given by the difference between Eq. (14.146) and Eq. (14.341):

$$\begin{aligned} E_T(C \equiv C, 2sp^3) &= E(C_{acetylene}, 2sp^3) - E(C, 2sp^3) \\ &= -16.20002 \text{ eV} - (-14.63489 \text{ eV}) \\ &= -1.56513 \text{ eV} \end{aligned} \quad (14.342)$$

As in the case of  $Cl_2$ , each  $H_2$ -type ellipsoidal MO comprises 75% of the  $C \equiv C$ -bond MO shared between two  $C2sp^3$  HOs corresponding to the electron charge density in Eq. (11.65) of  $\frac{-0.75e}{2}$ . But, the additional 25% charge-density contribution to each bond of the  $C \equiv C$ -

bond MO causes the electron charge density in Eq. (11.65) to be is given by  $\frac{-e}{2} = -0.5e$ . The

5 corresponding force constant  $k'$  to determine the ellipsoidal parameter  $c'$  in terms of the central force of the foci (Eq. (11.65)) is given by Eq. (14.152). The distance from the origin to each focus  $c'$  is given by Eq. (14.153). The internuclear distance is given by Eq. (14.154). The length of the semiminor axis of the prolate spheroidal  $C \equiv C$ -bond MO  $b = c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  
10  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of the  $C \equiv C$ -bond MO. From the energy equation and the relationship between the axes, the dimensions of the  $C \equiv C$ -bond MO are solved.

The general equations for the energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  of the  $C \equiv C$ -bond MO are the same as those of the  $CH$  MO except that energy of the  $C_{acetylene}2sp^3$   
15 HO is used and the triple-bond nature is considered. In the case of a single bond, the prolate spheroidal  $H_2$ -type MO transitions to the  $C_{acetylene}2sp^3$  HO of each carbon, and the energy of the  $C_{acetylene}2sp^3$  shell must remain constant and equal to the  $E(C_{acetylene}, 2sp^3)$  given by Eq. (14.391). Thus, the energy  $E(C_{acetylene}, 2sp^3)$  in Eq. (14.391) adds to that of the energies of the corresponding  $H_2$ -type ellipsoidal MO. The second and third bonds of the triple  $C \equiv C$ -  
20 bond MO also transition to each  $C_{acetylene}2sp^3$  HO of each  $C$ . The energy of a second and a third  $H_2$ -type ellipsoidal MO adds to the first energy component, and the three bonds achieve an energy minimum as a linear combination of the three  $H_2$ -type ellipsoidal MOs each having the carbon nuclei as the foci. Each  $C-C$ -bond MO comprises the same  $C_{acetylene}2sp^3$  HO shells of constant energy given by Eq. (14.391). As in the case of the water,  $NH_2$ ,  
25 ammonia, and ethylene molecules given by Eqs. (13.180), (13.320), (13.372), and (14.251), respectively, the energy of the redundant shell is subtracted from the total energy of the linear combination of the  $\sigma$  MO. Thus, the total energy  $E_T(C \equiv C, \sigma)$  of the  $\sigma$  component of the  $C \equiv C$ -bond MO is given by the sum of the energies of the three bonds each comprising the

linear combination of the  $C_{acetylene} 2sp^3$  HO and the  $H_2$ -type ellipsoidal MO as given by Eq. (14.337) wherein the  $E_T$  terms add positively and the  $E(C_{acetylene}, 2sp^3)$  term is positive due to the sum over a negative and two positive terms. Using Eqs. (13.431) and (14.341),  $E_T(C \equiv C, \sigma)$  is given by

$$\begin{aligned}
 E_T(C \equiv C, \sigma) &= E_T + E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) \\
 &= -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - E(C_{acetylene}, 2sp^3) \\
 &= -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] + 16.20002 \text{ eV}
 \end{aligned}
 \tag{14.343}$$

The total energy term of the double  $C \equiv C$ -bond MO is given by the sum of the three  $H_2$ -type ellipsoidal MOs given by Eq. (11.212). To match this boundary condition,  $E_T(C \equiv C, \sigma)$  given by Eq. (14.343) is set equal to three times Eq. (13.75):

$$E_T(C \equiv C, \sigma) = -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] + 16.20002 \text{ eV} = -94.90610 \text{ eV}
 \tag{14.344}$$

From the energy relationship given by Eq. (14.344) and the relationship between the axes given by Eqs. (14.153-14.154) and (13.62-13.63), the dimensions of the  $C \equiv C$ -bond MO can be solved.

Substitution of Eq. (14.153) into Eq. (14.344) gives

$$\frac{3e^2}{8\pi\epsilon_0 \sqrt{aa_0}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}} - 1 \right] = e111.10613
 \tag{14.345}$$

The most convenient way to solve Eq. (14.345) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.28714a_0 = 6.81122 \times 10^{-11} \text{ m}
 \tag{14.346}$$

Substitution of Eq. (14.346) into Eq. (14.153) gives

$$c' = 1.13452a_0 = 6.00362 \times 10^{-11} \text{ m}
 \tag{14.347}$$

The internuclear distance given by multiplying Eq. (14.347) by two is

$$2c' = 2.26904a_0 = 1.20072 \times 10^{-10} \text{ m}
 \tag{14.348}$$

The experimental bond distance is [3]

$$2c' = 1.203 \times 10^{-10} \text{ m}
 \tag{14.349}$$

Substitution of Eqs. (14.346-14.347) into Eq. (13.62) gives

$$b = c = 0.60793a_0 = 3.21704 \times 10^{-11} \text{ m} \quad (14.350)$$

Substitution of Eqs. (14.346-14.347) into Eq. (13.63) gives

$$e = 0.88143 \quad (14.351)$$

5 The nucleus of the  $C$  atoms comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{acetylene} 2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{acetylene 2sp^3} = 0.83008a_0$  is the radius of the  $C_{acetylene} 2sp^3$  shell. Substitution of Eqs. (14.346-14.347) into Eq. (13.261) gives

$$10 \quad \theta' = 137.91^\circ \quad (14.352)$$

Then, the angle  $\theta_{C \equiv C_{acetylene} 2sp^3 HO}$  the radial vector of the  $C 2sp^3$  HO makes with the internuclear axis is

$$\theta_{C \equiv C_{acetylene} 2sp^3 HO} = 180^\circ - 137.91^\circ = 42.09^\circ \quad (14.353)$$

as shown in Figure 43.

15

Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C \equiv C_{acetylene}, H_2 MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with each  $C_{acetylene} 2sp^3$  radial vector obeys the following

20 relationship:

$$r_{acetylene 2sp^3} \sin \theta_{C \equiv C_{acetylene} 2sp^3 HO} = 0.83008a_0 \sin \theta_{C \equiv C_{acetylene} 2sp^3 HO} = b \sin \theta_{C \equiv C_{acetylene}, H_2 MO} \quad (14.354)$$

such that

$$\theta_{C \equiv C_{acetylene}, H_2 MO} = \sin^{-1} \frac{0.83008a_0 \sin \theta_{C \equiv C_{acetylene} 2sp^3 HO}}{b} = \sin^{-1} \frac{0.83008a_0 \sin 42.09^\circ}{b} \quad (14.355)$$

with the use of Eq. (14.353). Substitution of Eq. (14.350) into Eq. (14.355) gives

$$25 \quad \theta_{C \equiv C_{acetylene}, H_2 MO} = 66.24^\circ \quad (14.356)$$

Then, the distance  $d_{C \equiv C_{acetylene}, H_2 MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C \equiv C_{acetylene}, H_2 MO} = a \cos \theta_{C \equiv C_{acetylene}, H_2 MO} \quad (14.357)$$

Substitution of Eqs. (14.346) and (14.356) into Eq. (14.357) gives

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$$d_{C \equiv C_{\text{acetylene}}, H_2 MO} = 0.51853 a_0 = 2.74396 \times 10^{-11} \text{ m} \quad (14.358)$$

The distance  $d_{C \equiv C_{\text{acetylene}}, 2sp^3 HO}$  along the internuclear axis from the origin of the  $C$  atom to the point of intersection of the orbitals is given by

$$d_{C \equiv C_{\text{acetylene}}, 2sp^3 HO} = c' - d_{C \equiv C_{\text{acetylene}}, H_2 MO} \quad (14.359)$$

5 Substitution of Eqs. (14.347) and (14.358) into Eq. (14.359) gives

$$d_{C \equiv C_{\text{acetylene}}, 2sp^3 HO} = 0.61599 a_0 = 3.25966 \times 10^{-11} \text{ m} \quad (14.360)$$

## FORCE BALANCE OF THE $CH$ MOs OF ACETYLENE

The  $C-H$  bond of each of the two equivalent  $CH$  MOs must comprise 75% of a  $H_2$ -type  
10 ellipsoidal MO and a  $C2sp^3$  HO as given by Eq. (13.429):

$$1 C2sp^3 + 0.75 H_2 MO \rightarrow CH MO \quad (14.361)$$

The force balance of the  $CH$  MO is determined by the boundary conditions that arise from  
15 the linear combination of orbitals according to Eq. (13.429) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant  $k'$  to determine the ellipsoidal parameter  $c'$  of the each  $H_2$ -type-ellipsoidal-MO component of the  $CH$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each  $C-H$ -bond MO to each focus  $c'$  is given  
20 by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal  $C-H$ -bond MO  $b = c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of each  $C-H$ -bond MO. From the energy equation and the relationship between the axes, the dimensions of the  
25  $CH$  MO are solved.

Consider the formation of the triple  $C \equiv C$ -bond MO of acetylene from two  $CH$  radicals, each having a  $C2sp^3$  shell with an energy given by Eq. (14.146). The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  are the same as those of the hydrogen carbide radical, except that two times  $E_T(C \equiv C, 2sp^3)$  is subtracted from  $E_T(CH)$  of Eq. (13.495). The  
30 subtraction of the energy change of the  $C2sp^3$  shells with the formation of the  $C \equiv C$ -bond

MO matches the energy of the  $C-H$ -bond MOs to the decrease in the energy of the  $C2sp^3$  HOs. Using Eqs. (13.495) and (14.342),  $E_{T_{acetylene}}(CH)$  is given by

$$E_{T_{acetylene}}(CH) = E_T + E(C, 2sp^3) - 2E_T(C \equiv C, 2sp^3) \\ = \left( -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \right. \\ \left. -14.63489 \text{ eV} - (-3.13026 \text{ eV}) \right) \quad (14.362)$$

$E_{T_{acetylene}}(CH)$  given by Eq. (14.362) is set equal to the energy of the  $H_2$ -type ellipsoidal MO

5 given by Eq. (13.75):

$$E_{T_{acetylene}}(CH) = \left( -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \right. \\ \left. -14.63489 \text{ eV} - (-3.13026 \text{ eV}) \right) = -31.63537 \text{ eV} \quad (14.363)$$

From the energy relationship given by Eq. (14.363) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH$  MO can be solved.

10 Substitution of Eq. (13.60) into Eq. (14.363) gives

$$\frac{e^2}{8\pi\epsilon_0 \sqrt{\frac{2aa_0}{3}}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right] = e20.13074 \quad (14.364)$$

The most convenient way to solve Eq. (14.364) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.48719a_0 = 7.86987 \times 10^{-11} \text{ m} \quad (14.365)$$

15 Substitution of Eq. (14.365) into Eq. (14.60) gives

$$c' = 0.99572a_0 = 5.26913 \times 10^{-11} \text{ m} \quad (14.366)$$

The internuclear distance given by multiplying Eq. (14.366) by two is

$$2c' = 1.99144a_0 = 1.05383 \times 10^{-10} \text{ m} \quad (14.367)$$

The experimental bond distance is [3]

$$20 \quad 2c' = 1.060 \times 10^{-10} \text{ m} \quad (14.368)$$

Substitution of Eqs. (14.365-14.366) into Eq. (14.62) gives

$$b = c = 1.10466a_0 = 5.84561 \times 10^{-11} \text{ m} \quad (14.369)$$

Substitution of Eqs. (14.365-14.366) into Eq. (14.63) gives

$$e = 0.66953 \quad (14.370)$$

The nucleus of the  $H$  atom and the nucleus of the  $C$  atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{acetylene}2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  
 5  $r_n = r_{acetylene2sp^3} = 0.83008a_0$  is the radius of the  $C_{acetylene}2sp^3$  shell. Substitution of Eqs. (14.365-14.366) into Eq. (13.261) gives

$$\theta' = 90.99^\circ \quad (14.371)$$

Then, the angle  $\theta_{C-H_{acetylene}2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$10 \quad \theta_{C-H_{acetylene}2sp^3HO} = 180^\circ - 90.99^\circ = 89.01^\circ \quad (14.372)$$

as shown in Figure 43. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-H_{acetylene},H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{acetylene}2sp^3$  radial vector obeys the following relationship:

$$15 \quad r_{acetylene2sp^3} \sin \theta_{C-H_{acetylene}2sp^3HO} = 0.83008a_0 \sin \theta_{C-H_{acetylene}2sp^3HO} = b \sin \theta_{C-H_{acetylene},H_2MO} \quad (14.373)$$

such that

$$\theta_{C-H_{acetylene},H_2MO} = \sin^{-1} \frac{0.83008a_0 \sin \theta_{C-H_{acetylene}2sp^3HO}}{b} = \sin^{-1} \frac{0.83008a_0 \sin 89.01^\circ}{b} \quad (14.374)$$

with the use of Eq. (14.372). Substitution of Eq. (14.369) into Eq. (14.374) gives

$$\theta_{C-H_{acetylene},H_2MO} = 48.71^\circ \quad (14.375)$$

20 Then, the distance  $d_{C-H_{acetylene},H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{acetylene},H_2MO} = a \cos \theta_{C-H_{acetylene},H_2MO} \quad (14.376)$$

Substitution of Eqs. (14.365) and (14.375) into Eq. (14.376) gives

$$d_{C-H_{acetylene},H_2MO} = 0.98145a_0 = 5.19359 \times 10^{-11} m \quad (14.377)$$

25 The distance  $d_{C-H_{acetylene}2sp^3HO}$  along the internuclear axis from the origin of the  $C$  atom to the point of intersection of the orbitals is given by

$$d_{C-H_{acetylene}2sp^3HO} = c' - d_{C-H_{acetylene},H_2MO} \quad (14.378)$$

Substitution of Eqs. (14.366) and (14.377) into Eq. (14.378) gives



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$$d_{C-H_{acetylene} 2sp^3 HO} = 0.01427a_0 = 7.55329 \times 10^{-13} m \quad (14.379)$$

With the  $C \equiv C$  double bond along one axis; the minimum energy is obtained with the  $C-H$ -bond MO at a maximum separation. Thus, the bond angle  $\theta_{C \equiv C-H}$  between the internuclear axis of the  $C \equiv C$  bond and the  $H$  atom of the  $CH$  groups is

$$\theta_{C \equiv C-H} = 180^\circ \quad (14.380)$$

The experimental angle between the  $C \equiv C-H$  bonds is [6]

$$\theta_{C \equiv C-H} = 180^\circ \quad (14.381)$$

The  $CHCH$  MO shown in Figure 44 was rendered using these parameters.

The charge-density in the  $C \equiv C$ -bond MO is increased by a factor of 0.25 per bond with the formation of the  $C_{acetylene} 2sp^3$  HOs each having a smaller radius. Using the orbital composition of the  $CH$  groups (Eq. (14.361)) and the  $C \equiv C$ -bond MO (Eq. (14.337), the radii of  $C1s = 0.17113a_0$  (Eq. (10.51)) and  $C_{acetylene} 2sp^3 = 0.83008a_0$  (Eq. (14.339)) shells, and the parameters of the  $C \equiv C$ -bond (Eqs. (13.3-13.4), (14.346-14.348), and (14.350-14.360)), the parameters of the  $C-H$ -bond MOs (Eqs. (13.3-13.4), (14.365-14.367), and (14.369-14.379)), and the bond-angle parameter (Eqs. (14.380-14.381)), the charge-density of the  $CHCH$  MO comprising the linear combination of two  $C-H$ -bond MOs and a  $C \equiv C$ -bond MO bridging the two  $CH$  groups is shown in Figure 44. Each  $C-H$ -bond MO comprises a  $H_2$ -type ellipsoidal MO and a  $C_{acetylene} 2sp^3$  HO having the dimensional diagram shown in Figure 43. The  $C \equiv C$ -bond MO comprises a  $H_2$ -type ellipsoidal MO bridging two  $C_{acetylene} 2sp^3$  HOs having the dimensional diagram also shown in Figure 43.

## ENERGIES OF THE $CH$ GROUPS

The energies of each  $CH$  group of acetylene are given by the substitution of the semiprincipal axes (Eqs. (14.365-14.366) and (14.369)) into the energy equations of hydrogen carbide (Eqs. (13.510-13.514)), with the exception that two times  $E_T(C \equiv C, 2sp^3)$  (Eq. (14.342)) is subtracted from  $E_T(CH)$  in Eq. (13.514):

$$V_e = (0.91771) \frac{-2e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -40.62396 eV \quad (14.382)$$

$$V_p = \frac{e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} = 13.66428 eV \quad (14.383)$$

$$T = (0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 13.65796 \text{ eV} \quad (14.384)$$

$$V_m = (0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -6.82898 \text{ eV} \quad (14.385)$$

$$E_{T_{\text{acetylene}}}(CH) = \left( \begin{aligned} & -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \\ & -14.63489 \text{ eV} - (-3.13026 \text{ eV}) \end{aligned} \right) = -31.63532 \text{ eV}$$

(14.386)

5 where  $E_{T_{\text{acetylene}}}(CH)$  is given by Eq. (14.362) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

## VIBRATION OF THE $^{12}CH$ GROUPS

The vibrational energy levels of  $CH$  in acetylene may be solved using the methods given in  
10 the Vibration and Rotation of  $CH$  section.

## THE DOPPLER ENERGY TERMS OF THE $^{12}CH$ GROUPS

The equations of the radiation reaction force of the  $CH$  groups in acetylene are the same as those of the hydrogen carbide radical with the substitution of the  $CH$ -group parameters.

15 Using Eq. (13.477), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 3.08370 \times 10^{16} \text{ rad/s} \quad (14.387)$$

where  $b$  is given by Eq. (14.369). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 3.08370 \times 10^{16} \text{ rad/s} = 20.29747 \text{ eV} \quad (14.388)$$

20 In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (14.388) for  $\bar{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(20.29747 \text{ eV})}{m_e c^2}} = -0.28197 \text{ eV} \quad (14.389)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $CH$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding  
 5 energies,  $\bar{E}_D$  given by Eq. (14.389) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of each  $C-H$  bond. Using  $\omega_e$  given by Eq. (13.458) for  $\bar{E}_{Kvib}$  of the transition state,  $\bar{E}_{acetylene\ osc} (^{12}CH)$  is

$$\bar{E}_{acetylene\ osc} (^{12}CH) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (14.390)$$

$$\bar{E}_{acetylene\ osc} (^{12}CH) = -0.28197\ eV + \frac{1}{2} (0.35532\ eV) = -0.10430\ eV \quad (14.391)$$

10

### TOTAL AND DIFFERENCE ENERGIES OF THE $^{12}CH$ GROUPS

$E_{acetyleneT+osc} (^{12}CH)$ , the total energy of each  $^{12}CH$  group including the Doppler term, is given by the sum of  $E_{T_{acetylene}} (CH)$  (Eq. (14.386)) and  $\bar{E}_{acetylene\ osc} (^{12}CH)$  given by Eq. (14.391):

$$\begin{aligned} E_{acetyleneT+osc} (CH) &= \left( V_e + T + V_m + V_p + E(C, 2sp^3) \right. \\ &\quad \left. - 2E_T (C \equiv C, 2sp^3) + \bar{E}_{acetylene\ osc} (^{12}CH) \right) \\ &= E_{T_{acetylene}} (CH) + \bar{E}_{acetylene\ osc} (^{12}CH) \end{aligned} \quad (14.392)$$

15

$$\begin{aligned} E_{acetyleneT+osc} (^{12}CH) &= \left\{ \begin{aligned} &\left( \frac{-e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \right) \\ &-14.63489\ eV - (-3.13026\ eV) \end{aligned} \right\} \\ &\quad \left\{ \begin{aligned} &\left( (31.63536831\ eV) \sqrt{\frac{2\hbar \sqrt{\frac{3}{4} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}} \right) \end{aligned} \right\} \\ &= -31.63537\ eV - \left( 0.28197\ eV - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \end{aligned} \quad (14.393)$$

From Eqs. (14.391-14.393), the total energy of each  $^{12}CH$  is

$$\begin{aligned}
E_{acetyleneT+osc}({}^{12}CH) &= -31.63537 \text{ eV} + \bar{E}_{acetylene\ osc}({}^{12}CH) \\
&= -31.63537 \text{ eV} - \left( 0.28197 \text{ eV} - \frac{1}{2}(0.35532 \text{ eV}) \right) \\
&= -31.73967 \text{ eV}
\end{aligned} \tag{14.394}$$

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

The total energy for each hydrogen carbide radical given by Eq. (13.485) is

$$\begin{aligned}
E_{radicalT+osc}({}^{12}CH) &= -31.63537 \text{ eV} + \bar{E}_{radicalosc}({}^{12}CH) \\
&= -31.63537 \text{ eV} - 0.24966 \text{ eV} + \frac{1}{2}(0.35532 \text{ eV}) \\
&= -31.70737 \text{ eV}
\end{aligned} \tag{14.395}$$

5 The difference in energy between the  $CH$  groups and the hydrogen carbide radical  $\Delta E_{T+osc}({}^{12}CH)$  is given by two times the difference between Eqs. (14.394) and (14.395):

$$\begin{aligned}
\Delta E_{T+osc}({}^{12}CH) &= 2(E_{acetyleneT+osc}({}^{12}CH) - E_{radicalT+osc}({}^{12}CH)) \\
&= 2(-31.73967 \text{ eV} - (-31.70737 \text{ eV})) \\
&= -0.06460 \text{ eV}
\end{aligned} \tag{14.396}$$

## SUM OF THE ENERGIES OF THE $C \equiv C$ $\sigma$ MO AND THE HOs OF ACETYLENE

The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  of the  $C \equiv C$  -bond MO are the same as those of the  $CH$  MO except that each term is multiplied by three corresponding to the triple bond and the energy term corresponding to the  $C_{acetylene} 2sp^3$  HOs in the equation for  $E_T$  is positive. The energies of each  $C \equiv C$  -bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.346-14.347) and (14.350)) into three times the energy equations of the  $CH$  MO (Eqs. (13.449-13.453)), with the exception that  $E(C, 2sp^3)$  in Eq. (13.453) is positive and given by Eq. (14.341):

$$V_e = 3(0.91771) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -182.53826 \text{ eV} \tag{14.397}$$

$$V_p = 3 \frac{e^2}{8\pi\epsilon_0\sqrt{a^2 - b^2}} = 35.97770 \text{ eV} \tag{14.398}$$

$$T = 3(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 70.90876 \text{ eV} \quad (14.399)$$

$$V_m = 3(0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -35.45438 \text{ eV} \quad (14.400)$$

$$E_T(C \equiv C, \sigma) = -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + 16.20002 \text{ eV} = -94.90616 \text{ eV} \quad (14.401)$$

5 where  $E_T(C \equiv C, \sigma)$  is the total energy of the  $C \equiv C$   $\sigma$  MO given by Eq. (14.343) which is reiteratively matched to three times Eq. (13.75) within five-significant-figure round off error.

The total energy of the  $C \equiv C$  -bond MO,  $E_T(C \equiv C)$ , is given by the sum of two times  $E_T(C \equiv C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell due to the decrease in radius with the formation of the  $C \equiv C$  -bond MO (Eq. (14.342)), and  $E_T(C \equiv C, \sigma)$ , the  $\sigma$  MO

10 contribution given by Eq. (14.344):

$$\begin{aligned} E_T(C \equiv C) &= 2E_T(C \equiv C, 2sp^3) + E_T(C \equiv C, \sigma) \\ &= \left( 2(-1.56513 \text{ eV}) + \left( -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + 16.20002 \text{ eV} \right) \right) \\ &= 2(-1.56513 \text{ eV}) + (-94.90610 \text{ eV}) \\ &= -98.03637 \text{ eV} \end{aligned} \quad (14.402)$$

## VIBRATION OF ACETYLENE

15 The vibrational energy levels of  $CHCH$  may be solved as two equivalent coupled harmonic oscillators with a bridging harmonic oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

# THE DOPPLER ENERGY TERMS OF THE $C \equiv C$ -BOND MO OF ACETYLENE

The equations of the radiation reaction force of the  $C \equiv C$ -bond MO are given by Eq. (14.231), except that the  $C \equiv C$ -bond MO parameters are used. The angular frequency of the  
5 reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.5e^2}{4\pi\epsilon_0 a^3}} = 2.00186 \times 10^{16} \text{ rad/s} \quad (14.403)$$

where  $a$  is given by Eq. (14.346). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.00186 \times 10^{16} \text{ rad/s} = 13.17659 \text{ eV} \quad (14.404)$$

10 In Eq. (11.181), substitution of  $E_T(C \equiv C)/3$  (Eq. (14.402)) for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (14.404) for  $\bar{E}_K$  gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -32.67879 \text{ eV} \sqrt{\frac{2e(13.17659 \text{ eV})}{m_e c^2}} = -0.23468 \text{ eV} \quad (14.405)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the  
15 transition state at their corresponding frequency. The decrease in the energy of the  $C \equiv C$ -bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (14.405) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of the  $C \equiv C$  bond. Using the experimental  
20  $C \equiv C$   $E_{vib}(\nu_3)$  of  $3374 \text{ cm}^{-1}$  ( $0.41833 \text{ eV}$ ) [6] for  $\bar{E}_{Kvib}$  of the transition state having three bonds,  $\bar{E}'_{osc}(C \equiv C, \sigma)$  per bond is

$$\bar{E}'_{osc}(C \equiv C, \sigma) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (14.406)$$

$$\bar{E}'_{osc}(C \equiv C, \sigma) = -0.23468 \text{ eV} + \frac{1}{2} (0.41833 \text{ eV}) = -0.02551 \text{ eV} \quad (14.407)$$

Given that the vibration and reentrant oscillation is for three  $C-C$  bonds of the  $C \equiv C$  triple  
25 bond,  $\bar{E}_{acetylene \text{ osc}}(C \equiv C, \sigma)$ , is:

$$\begin{aligned}
\bar{E}_{acetylene\ osc}(C \equiv C, \sigma) &= 3 \left( \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \\
&= 3 \left( -0.23468\ eV + \frac{1}{2} (0.41833\ eV) \right) \\
&= -0.07654\ eV
\end{aligned} \tag{14.408}$$

### TOTAL ENERGIES OF THE $C \equiv C$ -BOND MO OF ACETYLENE

$E_{T+osc}(C \equiv C)$ , the total energy of the  $C \equiv C$  -bond MO including the Doppler term, is given

5 by the sum of  $E_T(C \equiv C)$  (Eq. (14.402)) and  $\bar{E}_{acetylene\ osc}(C \equiv C, \sigma)$  given by Eq. (14.408):

$$\begin{aligned}
E_{T+osc}(C \equiv C) &= \left( V_e + T + V_m + V_p - E(C_{acetylene}, 2sp^3) \right. \\
&\quad \left. + 2E_T(C \equiv C, 2sp^3) + \bar{E}_{acetylene\ osc}(C \equiv C, \sigma) \right) \\
&= E_T(C \equiv C, \sigma) + 2E_T(C \equiv C, 2sp^3) + \bar{E}_{acetylene\ osc}(C \equiv C, \sigma) \\
&= E_T(C \equiv C) + \bar{E}_{acetylene\ osc}(C \equiv C, \sigma)
\end{aligned} \tag{14.409}$$

$$\begin{aligned}
E_{T+osc}(C \equiv C) &= \left\{ \left( \frac{-3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \right) \right. \\
&\quad \left. - E(C_{acetylene}, 2sp^3) + 2E_T(C \equiv C, 2sp^3) \right\} \\
&= \left\{ \left( 1 + (3) \left( \frac{1}{3} \right) \sqrt{\frac{2\hbar \sqrt{\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a^3}}}}{m_e c^2}} \right) + 3 \left( \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \right\} \\
&= -98.03637\ eV - 3 \left( 0.23468\ eV - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)
\end{aligned} \tag{14.410}$$

From Eqs. (14.408-14.410), the total energy of the  $C \equiv C$  -bond MO is

$$\begin{aligned}
E_{T+osc}(C \equiv C) &= -94.90610\ eV + 2E_T(C \equiv C, 2sp^3) + \bar{E}_{acetylene\ osc}(C \equiv C, \sigma) \\
&= -94.90610\ eV + 2(-1.56513\ eV) - 3 \left( 0.23468\ eV - \frac{1}{2} (0.41833\ eV) \right) \\
&= -98.11291\ eV
\end{aligned} \tag{14.411}$$

where the experimental  $E_{vib}$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

BOND ENERGY OF THE  $C \equiv C$  BOND OF ACETYLENE

As in the case of  $^{12}CH_2$  and  $^{14}NH$ , the dissociation of the  $C \equiv C$  bond forms three unpaired electrons per central atom wherein the magnetic moments cannot all cancel. The energy per atom  $E(magnetic)$  is given by Eq. (13.524). Thus, the dissociation energy of the  $C \equiv C$  bond of  $CHCH$ ,  $E_D(HC \equiv CH)$ , is given by six times  $E(C, 2sp^3)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each  $CH$  radical that forms the triple  $C \equiv C$  bond, minus the sum of  $\Delta E_{T+osc}(^{12}CH)$  (Eq. (14.396)), the energy change going from the hydrogen carbide radicals to the  $CH$  groups of acetylene,  $E_{T+osc}(C \equiv C)$  (Eq. (14.411)), and two times  $E(magnetic)$  given by Eq. (13.524). Thus, the dissociation energy of the  $C \equiv C$  bond of  $CHCH$ , is

$$\begin{aligned} E_D(HC \equiv CH) &= 6(E(C, 2sp^3)) - (\Delta E_{T+osc}(^{12}CH) + E_{T+osc}(C \equiv C) + 2E(magnetic)) \\ &= 6(-14.63489 \text{ eV}) - (-0.06460 \text{ eV} - 98.11291 \text{ eV} + 0.29606 \text{ eV}) \quad (14.412) \\ &= 6(-14.63489 \text{ eV}) - (-97.88145 \text{ eV}) \\ &= 10.07212 \text{ eV} \end{aligned}$$

The experimental dissociation energy of the  $C \equiv C$  bond of  $CHCH$  is [7]

$$E_D(HC \equiv CH) = 10.0014 \text{ eV} \quad (14.413)$$

The results of the determination of bond parameters of  $CHCH$  are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

BENZENE MOLECULE ( $C_6H_6$ )

The benzene molecule  $C_6H_6$  is formed by the reaction of three ethylene molecules:



$C_6H_6$  can be solved using the same principles as those used to solve ethylene wherein the  $2s$  and  $2p$  shells of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each  $2sp^3$  HO of each carbon atom initially has four unpaired electrons. Thus, the 6  $H$  atomic orbitals (AOs) of benzene contribute six electrons and the six  $sp^3$ -hybridized carbon



atoms contribute twenty-four electrons to form six  $C-H$  bonds and six  $C=C$  bonds. Each  $C-H$  bond has two paired electrons with one donated from the  $H$  AO and the other from the  $C2sp^3$  HO. Each  $C=C$  bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two  $C2sp^3$  HOs of the participating carbon  
 5 atoms. Each  $C-H$  and each  $C=C$  bond comprises a linear combination of one and two diatomic  $H_2$ -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

### FORCE BALANCE OF THE $C=C$ -BOND MO OF BENZENE

10  $C_6H_6$  can be considered a linear combination of three ethylene molecules wherein a  $C-H$  bond of each  $CH_2$  group of  $H_2C=CH_2$  is replaced by a  $C=C$  bond to form a six-member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule ( $CH_2CH_2$ ) section. Before forming ethylene groups, the  $2sp^3$  hybridized orbital arrangement of each carbon atom is given by Eq. (14.140). The sum  $E_T(C, 2sp^3)$  of  
 15 calculated energies of  $C$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  is given by Eq. (14.141). The radius  $r_{2sp^3}$  of the  $C2sp^3$  shell is given by Eq. (14.142). The Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  and the energy  $E(C, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell are given by Eqs. (14.143) and (14.146), respectively. Two  $CH_2$  radicals bond to form  $CH_2CH_2$  by forming a MO between the two pairs of remaining  $C2sp^3$ -HO electrons of the two carbon atoms. However, in this  
 20 case, the sharing of electrons between four  $C2sp^3$  HOs to form a MO comprising four spin-paired electrons permits each  $C2sp^3$  HO to decrease in radius and energy. The  $C=C$  -bond MO is a prolate-spheroidal-MO surface that cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the  $C2sp^3$  shell  
 25 at each  $C$  atom. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of each  $C2sp^3$  shell. As in the case of previous examples of energy-matched MOs such as those of  $OH$ ,  $NH$ ,  $CH$ , the  $C=O$  -bond MO of  $CO_2$ , and the  $C-C$  -bond MO of  $CH_3CH_3$ , the  $C=C$  -bond MO of ethylene must comprise 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $C=C$  -bond MO must comprise

a linear combination of two MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

$$2(2 C2sp^3 + 0.75 H_2 MO) \rightarrow C = C - bond MO \quad (14.415)$$

5

The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution from each  $C2sp^3$  HO to the  $C = C$ -bond MO to achieve an energy minimum. The force balance of the  $C = C$ -bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.415) and the energy matching condition between the  $C2sp^3$ -HO components of the MO.

The sharing of electrons between two pairs of  $C2sp^3$  HOs to form a  $C = C$ -bond MO permits each participating hybridized orbital to decrease in radius and energy. The sum  $E_T(C_{ethylene}, 2sp^3)$  of calculated energies of  $C2sp^3$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  is given by Eq. (14.243). In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating  $C2sp^3$  HO donates an excess of 25% of its electron density to the  $C = C$ -bond MO to form an energy minimum. By considering this electron redistribution in the ethylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{ethylene 2sp^3}$  of the  $C2sp^3$  shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy  $E_{Coulomb}(C_{ethylene}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.245). The energy  $E(C_{ethylene}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.246).  $E_T(C = C, 2sp^3)$  (Eq. (14.247), the energy change of each  $C2sp^3$  shell with the formation of the  $C = C$ -bond MO is given by the difference between  $E(C_{ethylene}, 2sp^3)$  and  $E(C, 2sp^3)$ .

25

Consider the case where three sets of  $C = C$ -bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

$$\left( \begin{array}{l} 3(2 C2sp^3 + 0.75 H_2 MO) \rightarrow 3(C^{4e} = C) - \text{ethylene-type-bond MO} \\ \rightarrow 6(C^{3e} = C) - \text{bond MO of benzene} \end{array} \right) \quad (14.416)$$

The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further  
 5 comprises an excess 25% charge-density contribution per bond from each  $C2sp^3$  HO to the  
 $C = C$ -bond MO to achieve an energy minimum. Thus, the dimensional parameters of each  
 bond  $C = C$ -bond are determined using the same equations as those used to determine the  
 same parameters of the  $C = C$ -bond MO of ethylene (Eqs. (14.242-14.268)) while matching  
 the boundary conditions of the structure of benzene. The energies of each  $C = C$  bond of  
 10 benzene are also determined using the same equations as those of ethylene with the  
 parameters of benzene. The result is that the energies are essentially given as 0.75 times the  
 energies of the  $C = C$ -bond MO of ethylene (Eqs. (14.251-14.253) and (14.319-14.333)).

The derivation of the dimensional parameters of benzene follows the same procedure  
 as the determination of those of ethylene. As in the case of ethylene, each  $H_2$ -type  
 15 ellipsoidal MO comprises 75% of the  $C = C$ -bond MO shared between two  $C2sp^3$  HOs  
 corresponding to the electron charge density in Eq. (11.65) of  $\frac{-0.75e}{2}$ . But, the additional  
 25% charge-density contribution to each bond of the  $C = C$ -bond MO causes the electron  
 charge density in Eq. (11.65) to be is given by  $\frac{-e}{2} = -0.5e$ . The corresponding force constant  
 $k'$  is given by Eq. (14.152). In addition, the energy matching at all six  $C2sp^3$  HOs further  
 20 requires that  $k'$  be corrected by a hybridization factor (Eq. (13.430)) as in the case of  
 ethylene, expect that the constraint that the bonds connect a six-member ring of  $C = C$  bonds  
 of benzene rather two  $C2sp^3$  HOs of ethylene decreases the hybridization factor of benzene  
 compared to that of ethylene (Eq. (14.248)).

Since the energy of each  $H_2$ -type ellipsoidal MO is matched to that of all the  
 25 continuously connected  $C_{benzene}2sp^3$  HOs, the hybridization-energy-matching factor is  
 0.85252. Hybridization with 25% electron donation to each  $C = C$ -bond gives rise to the  
 $C_{benzene}2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(C_{benzene}, 2sp^3)$  given by Eq. (14.245). The  
 corresponding hybridization factor is given by the ratio of 15.95955 eV, the magnitude of

$E_{Coulomb}(C_{benzene}, 2sp^3)$  given by Eq. (14.245), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). The hybridization energy factor  $C_{benzeneC2sp^3HO}$  is

$$C_{benzeneC2sp^3HO} = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{benzene2sp^3}}} = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 0.85252 a_0}} = \frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252 \quad (14.417)$$

5 Thus, the force constant  $k'$  to determine the ellipsoidal parameter  $c'$  in terms of the central force of the foci (Eq. (11.65)) is given by

$$k' = C_{benzeneC2sp^3HO} \frac{(0.5)2e^2}{4\pi\epsilon_0} = 0.85252 \frac{(0.5)2e^2}{4\pi\epsilon_0} \quad (14.418)$$

The distance from the origin to each focus  $c'$  is given by substitution of Eq. (14.418) into Eq. (13.60). Thus, the distance from the origin of the component of the double  $C = C$  -bond MO  
10 to each focus  $c'$  is given by

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{(0.85252)m_e e^2 a}} = \sqrt{\frac{aa_0}{0.85252}} \quad (14.419)$$

The internuclear distance from Eq. (14.419) is

$$2c' = 2\sqrt{\frac{aa_0}{0.85252}} \quad (14.420)$$

The length of the semiminor axis of the prolate spheroidal  $C = C$  -bond MO  $b = c$  is given by  
15 Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of the  $C = C$  -bond MO. From the energy equation and the relationship between the axes, the dimensions of the  $C = C$  -bond MO are solved.

The general equations for the energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  of the  
20  $C = C$  -bond MO of benzene are the same as those of the  $CH_2CH_2$  MO except that energy of the  $C_{benzene}2sp^3$  HO is used and the hybridization factor is given by Eq. (14.417). Using Eqs. (14.251) and (14.417),  $E_T(C = C, \sigma)$  is given by

$$\begin{aligned} E_T(C = C, \sigma) &= E_T + E(C_{benzene}, 2sp^3) - E(C_{benzene}, 2sp^3) \\ &= -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.85252) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \end{aligned} \quad (14.421)$$

The total energy term of the double  $C = C$  -bond MO is given by the sum of the two  $H_2$  -type ellipsoidal MOs given by Eq. (11.212). To match this boundary condition,  $E_T(C = C, \sigma)$  given by Eq. (14.421) is set equal to two times Eq. (13.75):

$$E_T(C = C, \sigma) = -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.85252) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] = -63.27074 \text{ eV} \quad (14.422)$$

- 5 From the energy relationship given by Eq. (14.422) and the relationship between the axes given by Eqs. (14.419-14.420) and (13.62-13.63), the dimensions of the  $C = C$  -bond MO can be solved.

Substitution of Eq. (14.419) into Eq. (14.422) gives

$$\frac{2e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{0.85252}}} \left[ (0.85252) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{0.85252}}}{a - \sqrt{\frac{aa_0}{0.85252}}} - 1 \right] = 63.27074 \quad (14.423)$$

- 10 The most convenient way to solve Eq. (14.423) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.47348a_0 = 7.79733 \times 10^{-11} \text{ m} \quad (14.424)$$

Substitution of Eq. (14.424) into Eq. (14.4129) gives

$$c' = 1.31468a_0 = 6.95699 \times 10^{-11} \text{ m} \quad (14.425)$$

- 15 The internuclear distance given by multiplying Eq. (14.425) by two is

$$2c' = 2.62936a_0 = 1.39140 \times 10^{-10} \text{ m} \quad (14.426)$$

The experimental bond distance is [3]

$$2c' = 1.339 \times 10^{-10} \text{ m} \quad (14.427)$$

Substitution of Eqs. (14.424-14.425) into Eq. (13.62) gives

$$20 \quad b = c = 0.66540a_0 = 3.52116 \times 10^{-11} \text{ m} \quad (14.428)$$

Substitution of Eqs. (14.424-14.425) into Eq. (13.63) gives

$$e = 0.89223 \quad (14.429)$$

- The nucleus of the  $C$  atoms comprise the foci of the  $H_2$  -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$  -type ellipsoidal MO and the  $C_{\text{benzene}} 2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). Each benzene carbon atom contributes
- 25  $(0.75)(-1.13380 \text{ eV}) = -0.85035 \text{ eV}$  (Eqs. (14.483) and (14.493)) to each of the two  $C=C$  -bond MOs and  $(0.5)(-1.13380 \text{ eV}) = -0.56690 \text{ eV}$  (Eq. (14.467)) to the corresponding

$C-H$ -bond MO. The energy contribution due to the charge donation at each carbon superimposes linearly. The radius of  $r_{benzene\ 2sp^3} = 0.79597a_0$  is calculated using Eq. (14.518) using the total energy donation to each bond with which it is participates in bonding. The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{benzene\ 2sp^3} = 0.79597a_0$  is the

5 radius of the  $C_{benzene\ 2sp^3}$  shell. Substitution of Eqs. (14.424-14.425) into Eq. (13.261) gives

$$\theta' = 134.24^\circ \quad (14.430)$$

Then, the angle  $\theta_{C=C_{benzene\ 2sp^3}HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C=C_{benzene\ 2sp^3}HO} = 180^\circ - 134.24^\circ = 45.76^\circ \quad (14.431)$$

10 as shown in Figure 45.

Thus, the  $^{12}CH_4$  bond dissociation energy,  $E_D(^{12}CH_4)$ , given by Eqs. (13.154), and (13.614-13.616) is

$$\begin{aligned} E_D(^{12}CH_4) &= -(67.95529\ eV + 13.59844\ eV) - E_{T+osc}(^{12}CH_4) \\ &= -81.55373\ eV - (-86.04373\ eV) \\ &= 4.4900\ eV \end{aligned} \quad (13.617)$$

The experimental  $^{12}CH_4$  bond dissociation energy is [40]

$$15 \quad E_D(^{12}CH_4) = 4.48464\ eV \quad (13.618)$$

Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C=C_{benzene\ H_2MO}}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with each  $C_{benzene\ 2sp^3}$  radial vector obeys the following relationship:

$$20 \quad r_{benzene\ 2sp^3} \sin \theta_{C=C_{benzene\ 2sp^3}HO} = 0.79597a_0 \sin \theta_{C=C_{benzene\ 2sp^3}HO} = b \sin \theta_{C=C_{benzene\ H_2MO}} \quad (14.432)$$

such that

$$\theta_{C=C_{benzene\ H_2MO}} = \sin^{-1} \frac{0.79597a_0 \sin \theta_{C=C_{benzene\ 2sp^3}HO}}{b} = \sin^{-1} \frac{0.79597a_0 \sin 45.76^\circ}{b} \quad (14.433)$$

with the use of Eq. (14.431). Substitution of Eq. (14.428) into Eq. (14.433) gives

$$\theta_{C=C_{benzene\ H_2MO}} = 58.98^\circ \quad (14.434)$$

25 Then, the distance  $d_{C=C_{benzene\ H_2MO}}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C=C_{benzene}, H_2MO} = a \cos \theta_{C=C_{benzene}, H_2MO} \quad (14.435)$$

Substitution of Eqs. (14.424) and (14.434) into Eq. (14.435) gives

$$d_{C=C_{benzene}, H_2MO} = 0.75935a_0 = 4.01829 \times 10^{-11} \text{ m} \quad (14.436)$$

The distance  $d_{C=C_{benzene} 2sp^3HO}$  along the internuclear axis from the origin of the  $C$  atom to the point of intersection of the orbitals is given by

$$d_{C=C_{benzene} 2sp^3HO} = c' - d_{C=C_{benzene}, H_2MO} \quad (14.437)$$

Substitution of Eqs. (14.425) and (14.436) into Eq. (14.437) gives

$$d_{C=C_{benzene} 2sp^3HO} = 0.55533a_0 = 2.93870 \times 10^{-11} \text{ m} \quad (14.438)$$

## 10 FORCE BALANCE OF THE $CH$ MOs OF BENZENE

Benzene can also be considered as comprising chemical bonds between six  $CH$  radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of  $CH$  is given in the Hydrogen Carbide ( $CH$ ) section. Each  $C-H$  bond of  $CH$  having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75%  $H_2$ -type ellipsoidal MO and 25%  $C2sp^3$  HO as given by Eq. (13.439):



The proton of the  $H$  atom and the nucleus of the  $C$  atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , the  $C-H$ -bond MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the  $H$  proton that is continuous with the  $C2sp^3$  shell at the  $C$  atom whose nucleus serves as the other focus.

The force balance of the  $CH$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.439) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO. The force constant  $k'$  to determine the ellipsoidal parameter  $c'$  of the each  $H_2$ -type-ellipsoidal-MO component of the  $CH$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance

from the origin of each  $C-H$ -bond MO to each focus  $c'$  is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal  $C-H$ -bond MO  $b=c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other  
 5 axes of each prolate spheroid and eccentricity of each  $C-H$ -bond MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH$  MO are solved.

Consider the formation of the double  $C=C$ -bond MOs of benzene wherein ethylene formed from two  $CH_2$  radicals, each having a  $C2sp^3$  shell with an energy given by Eq. (14.146), serves as a basis element. The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  are  
 10 the same as those of the hydrogen carbide radical, except that  $E_T(C=C, 2sp^3)$  is subtracted from  $E_T(CH)$  of Eq. (13.495). As in the case of the  $CH_2$  groups of ethylene (Eq. (14.270)), the subtraction of the energy change of the  $C2sp^3$  shell per  $H$  with the formation of the  $C=C$ -bond MO matches the energy of each  $C-H$ -bond MO to the decrease in the energy of the corresponding  $C2sp^3$  HO. Using Eqs. (13.431) and (14.247),  $E_{T_{benzene}}(CH)$  is given by

$$\begin{aligned}
 E_{T_{benzene}}(CH) &= E_T + E(C, 2sp^3) - E_T(C=C, 2sp^3) \\
 15 \quad &= \left[ -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \right. \\
 &\quad \left. -14.63489 \text{ eV} - (-1.13379 \text{ eV}) \right] \quad (14.440)
 \end{aligned}$$

$E_{T_{benzene}}(CH)$  given by Eq. (14.440) is set equal to the energy of the  $H_2$ -type ellipsoidal MO given by Eq. (13.75):

$$\begin{aligned}
 E_{T_{benzene}}(CH) &= \left[ -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \right. \\
 &\quad \left. -14.63489 \text{ eV} - (-1.13379 \text{ eV}) \right] = -31.63537 \text{ eV} \\
 (14.441)
 \end{aligned}$$

20 From the energy relationship given by Eq. (14.441) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.441) gives

$$\frac{e^2}{8\pi\epsilon_0 \sqrt{\frac{2aa_0}{3}}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right] = e18.13427 \quad (14.442)$$



The most convenient way to solve Eq. (14.442) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.60061a_0 = 8.47006 \times 10^{-11} \text{ m} \quad (14.443)$$

Substitution of Eq. (14.443) into Eq. (14.60) gives

$$5 \quad c' = 1.03299a_0 = 5.46636 \times 10^{-11} \text{ m} \quad (14.444)$$

The internuclear distance given by multiplying Eq. (14.444) by two is

$$2c' = 2.06598a_0 = 1.09327 \times 10^{-10} \text{ m} \quad (14.445)$$

The experimental bond distance is [3]

$$2c' = 1.101 \times 10^{-10} \text{ m} \quad (14.446)$$

10 Substitution of Eqs. (14.443-14.444) into Eq. (14.62) gives

$$b = c = 1.22265a_0 = 6.47000 \times 10^{-11} \text{ m} \quad (14.447)$$

Substitution of Eqs. (14.443-14.444) into Eq. (14.63) gives

$$e = 0.64537 \quad (14.448)$$

The nucleus of the  $H$  atom and the nucleus of the  $C$  atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{benzene}2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{benzene2sp^3} = 0.79597a_0$  is the radius of the  $C_{benzene}2sp^3$  shell. Substitution of Eqs. (14.443-14.444) into Eq. (13.261) gives

$$20 \quad \theta' = 74.42^\circ \quad (14.449)$$

Then, the angle  $\theta_{C-H_{benzene}2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C-H_{benzene}2sp^3HO} = 180^\circ - 74.42^\circ = 105.58^\circ \quad (14.450)$$

as shown in Figure 46.

25

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-H_{benzene},H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{benzene}2sp^3$  radial vector obeys the following relationship:

$$30 \quad r_{benzene2sp^3} \sin \theta_{C-H_{benzene}2sp^3HO} = 0.79597a_0 \sin \theta_{C-H_{benzene}2sp^3HO} = b \sin \theta_{C-H_{benzene},H_2MO} \quad (14.451)$$

such that

$$\theta_{C-H_{benzene}, H_2MO} = \sin^{-1} \frac{0.79597a_0 \sin \theta_{C-H_{benzene} 2sp^3HO}}{b} = \sin^{-1} \frac{0.79597a_0 \sin 105.58^\circ}{b} \quad (14.452)$$

with the use of Eq. (14.450). Substitution of Eq. (14.447) into Eq. (14.452) gives

$$\theta_{C-H_{benzene}, H_2MO} = 38.84^\circ \quad (14.453)$$

- 5 Then, the distance  $d_{C-H_{benzene}, H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{benzene}, H_2MO} = a \cos \theta_{C-H_{benzene}, H_2MO} \quad (14.454)$$

Substitution of Eqs. (14.443) and (14.453) into Eq. (14.454) gives

$$d_{C-H_{benzene}, H_2MO} = 1.24678a_0 = 6.59767 \times 10^{-11} \text{ m} \quad (14.455)$$

- 10 The distance  $d_{C-H_{benzene} 2sp^3HO}$  along the internuclear axis from the origin of the  $C$  atom to the point of intersection of the orbitals is given by

$$d_{C-H_{benzene} 2sp^3HO} = d_{C-H_{benzene}, H_2MO} - c' \quad (14.456)$$

Substitution of Eqs. (14.444) and (14.455) into Eq. (14.456) gives

$$d_{C-H_{benzene} 2sp^3HO} = 0.21379a_0 = 1.13131 \times 10^{-11} \text{ m} \quad (14.457)$$

- 15 The basis set of benzene, the ethylene molecule, is planar with bond angles of approximately  $120^\circ$  (Eqs. (14.298-14.302)). To form a closed ring of equivalent planar bonds, the  $C=C$  bonds of benzene form a planar hexagon. The bond angle  $\theta_{C=C=C}$  between the internuclear axis of any two adjacent  $C=C$  bonds is

$$\theta_{C=C=C} = 120^\circ \quad (14.458)$$

- 20 The bond angle  $\theta_{C=C-H}$  between the internuclear axis of each  $C=C$  bond and the corresponding  $H$  atom of each  $CH$  group is

$$\theta_{C=C-H} = 120^\circ \quad (14.459)$$

The experimental angle between the  $C=C=C$  bonds is [13-15]

$$\theta_{C=C=C} = 120^\circ \quad (14.460)$$

- 25 The experimental angle between the  $C=C-H$  bonds is [13-15]

$$\theta_{C=C-H} = 120^\circ \quad (14.461)$$

The  $C_6H_6$  MO shown in Figure 47 was rendered using these parameters.

The charge-density in the  $C=C$ -bond MO is increased by a factor of 0.25 per bond with the formation of the  $C_{benzene} 2sp^3$  HOs each having a smaller radius. Using the orbital

composition of the  $CH$  groups (Eq. (14.439)) and the  $C = C$ -bond MO (Eq. (14.416), the radii of  $C1s = 0.17113a_0$  (Eq. (10.51)) and  $C_{benzene} 2sp^3 = 0.79597a_0$  (Eq. (14.520)) shells, and the parameters of the  $C = C$ -bond (Eqs. (13.3-13.4), (14.424-14.426), and (14.428-14.438)), the parameters of the  $C - H$ -bond MOs (Eqs. (13.3-13.4), (14.443-14.445), and  
 5 (14.447-14.457)), and the bond-angle parameters (Eqs. (14.458-14.459)), the charge-density of the  $C_6H_6$  MO comprising the linear combination of six sets of  $C - H$ -bond MOs with bridging  $C \equiv C$ -bond MOs is shown in Figure 47. Each  $C - H$ -bond MO comprises a  $H_2$ -type ellipsoidal MO and a  $C_{benzene} 2sp^3$  HO having the dimensional diagram shown in Figure 46. The  $C = C$ -bond MO comprises a  $H_2$ -type ellipsoidal MO bridging two sets of two  
 10  $C_{benzene} 2sp^3$  HOs having the dimensional diagram shown in Figure 45.

## ENERGIES OF THE $CH$ GROUPS

The energies of each  $CH$  group of benzene are given by the substitution of the semiprincipal axes (Eqs. (14.443-14.444) and (14.447)) into the energy equations of hydrogen carbide (Eqs.  
 15 (13.449-13.453)), with the exception that  $E_T(C = C, 2sp^3)$  (Eq. (14.247)) is subtracted from  $E_T(CH)$  in Eq. (13.453):

$$V_e = (0.91771) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -37.10024 \text{ eV} \quad (14.462)$$

$$V_p = \frac{e^2}{8\pi\epsilon_0\sqrt{a^2 - b^2}} = 13.17125 \text{ eV} \quad (14.463)$$

$$T = (0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 11.58941 \text{ eV} \quad (14.464)$$

$$20 \quad V_m = (0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -5.79470 \text{ eV} \quad (14.465)$$

$$E_{T_{benzene}}(CH) = \left( \frac{-\frac{e^2}{8\pi\epsilon_0 c'}}{\left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right]} \right) = -31.63539 \text{ eV} \\ (14.466)$$

where  $E_{T_{benzene}}(CH)$  is given by Eq. (14.440) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

The total energy of the  $C-H$ -bond MO,  $E_{T_{benzene}}(C-H)$ , is given by the sum of  $0.5E_T(C=C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell per single bond due to the decrease in radius with the formation of the corresponding  $C=C$ -bond MO (Eq. (14.247)), and  $E_{T_{benzene}}(CH)$ , the  $\sigma$  MO contribution given by Eq. (14.441):

$$\begin{aligned}
 E_{T_{benzene}}(C-H) &= (0.5)E_T(C=C, 2sp^3) + E_{T_{benzene}}(CH) \\
 &= \left( (0.5)(-1.13379 \text{ eV}) + \left( -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \right) \right) \\
 &= (0.5)(-1.13379 \text{ eV}) + (-31.63537 \text{ eV}) \\
 &= -32.20226 \text{ eV}
 \end{aligned} \tag{14.467}$$

## VIBRATION OF THE $^{12}CH$ GROUPS

The vibrational energy levels of  $CH$  in benzene may be solved using the methods given in the Vibration and Rotation of  $CH$  section.

## THE DOPPLER ENERGY TERMS OF THE $^{12}CH$ GROUPS

The equations of the radiation reaction force of the  $CH$  groups in benzene are the same as those of the hydrogen carbide radical with the substitution of the  $CH$ -group parameters. Using Eq. (13.477), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 2.64826 \times 10^{16} \text{ rad/s} \tag{14.468}$$

where  $b$  is given by Eq. (14.447). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.64826 \times 10^{16} \text{ rad/s} = 17.43132 \text{ eV} \tag{14.469}$$

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (14.469) for  $\bar{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

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$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(17.43132 \text{ eV})}{m_e c^2}} = -0.26130 \text{ eV} \quad (14.470)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $CH$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (14.470) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of the  $C-H$  bond. Using  $\omega_e$  given by Eq. (13.458) for  $\bar{E}_{Kvib}$  of the transition,  $\bar{E}_{benzene\ osc} (^{12}CH)$  per bond is

$$\bar{E}_{benzene\ osc} (^{12}CH) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (14.471)$$

$$10 \quad \bar{E}_{benzene\ osc} (^{12}CH) = -0.26130 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) = -0.08364 \text{ eV} \quad (14.472)$$

## TOTAL AND BOND ENERGIES OF THE $^{12}CH$ GROUPS

$E_{benzeneT+osc} (^{12}CH)$ , the total energy of each  $^{12}CH$  group including the Doppler term, is given by the sum of  $E_{T_{benzene}} (C-H)$  (Eq. (14.467)) and  $\bar{E}_{benzene\ osc} (^{12}CH)$  given by Eq. (14.472):

$$15 \quad E_{benzeneT+osc} (CH) = \left\{ \begin{aligned} & \left( (V_e + T + V_m + V_p + E(C, 2sp^3) - E_T(C=C, 2sp^3)) \right) \\ & + 0.5 E_T(C=C, 2sp^3) + \bar{E}_{benzene\ osc} (^{12}CH) \end{aligned} \right\} \quad (14.473)$$

$$= E_{T_{benzene}} (C-H) + \bar{E}_{benzene\ osc} (^{12}CH)$$

$$E_{benzeneT+osc} (^{12}CH) = \left\{ \begin{aligned} & \left( \frac{-e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 0.5(1.13379 \text{ eV}) \right. \\ & \left. - 14.63489 \text{ eV} - (-1.13379 \text{ eV}) \right) \\ & - \left( (31.63536831 \text{ eV}) \sqrt{\frac{2\hbar \sqrt{\frac{3}{4} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2}} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \end{aligned} \right\}$$

$$= -32.20226 \text{ eV} - \left( 0.26130 \text{ eV} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \quad (14.474)$$

From Eqs. (14.472-14.474), the total energy of each  $^{12}CH$  is

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$$\begin{aligned}
 E_{benzeneT+osc} (^{12}CH) &= -32.20226 \text{ eV} + \bar{E}_{benzene\ osc} (^{12}CH_2) \\
 &= -32.20226 \text{ eV} - \left( 0.26130 \text{ eV} - \frac{1}{2}(0.35532 \text{ eV}) \right) \\
 &= -32.28590 \text{ eV}
 \end{aligned} \tag{14.475}$$

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

As in the case of  $^{12}CH_2$ ,  $^{14}NH$ , and acetylene, the dissociation of the  $C=C$  bonds forms three unpaired electrons per central atom wherein the magnetic moments cannot all cancel. The energy per atom  $E(magnetic)$  is given by Eq. (13.524). Thus, the bond dissociation energy of each  $CH$  group of the linear combination to form benzene,  $E_{D_{benzene}} (^{12}CH)$ , is given by the sum of the total energies of the  $C2sp^3$  HO and the hydrogen atom minus the sum of  $E_{benzeneT+osc} (^{12}CH)$  and  $E(magnetic)$  given by Eq. (13.524):

$$E_{D_{benzene}} (^{12}CH) = E(C, 2sp^3) + E(H) - (E_{benzeneT+osc} (^{12}CH) + E(magnetic)) \tag{14.476}$$

$E(C, 2sp^3)$  is given by Eq. (13.428),  $E_D(H)$  is given by Eq. (13.154), and  $E(magnetic)$  is given by Eq. (13.524). Thus,  $E_{D_{benzene}} (^{12}CH)$  given by Eqs. (13.154), (13.428), (13.524), (14.475), and (14.476) is

$$\begin{aligned}
 E_{D_{benzene}} (^{12}CH) &= -(14.63489 \text{ eV} + 13.59844 \text{ eV}) - (E_{benzeneT+osc} (CH) + E(magnetic)) \\
 &= -28.23333 \text{ eV} - (-32.28590 \text{ eV} + 0.14803 \text{ eV}) \\
 &= 3.90454 \text{ eV}
 \end{aligned} \tag{14.477}$$

## 15 SUM OF THE ENERGIES OF THE $C=C$ $\sigma$ MO ELEMENT AND THE HOS OF BENZENE

The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  of the  $C=C$ -bond MO of benzene are the same as those of the  $CH_2CH_2$  MO except that the hybridization factor is given by Eq. (14.417). The energies of each  $C=C$ -bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.424-14.425) and (14.428)) into energy equations of the  $CH_2CH_2$  MO (Eqs. (14.319-14.323)), with the exception that the hybridization factor is 0.85252 (Eq. (14.417)):

$$V_e = 2(0.85252) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -101.12679 \text{ eV} \tag{14.478}$$

$$V_p = 2 \frac{e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} = 20.69825 \text{ eV} \quad (14.479)$$

$$T = 2(0.85252) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 34.31559 \text{ eV} \quad (14.480)$$

$$V_m = 2(0.85252) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -17.15779 \text{ eV} \quad (14.481)$$

$$E_T(C = C, \sigma) = -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.85252) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] = -63.27075 \text{ eV} \quad (14.482)$$

5 where  $E_T(C = C, \sigma)$  is the total energy of the  $C = C$   $\sigma$  MO given by Eq. (14.421) which is reiteratively matched to two times Eq. (13.75) within five-significant-figure round off error.

The total energy of the  $C = C$  -bond MO,  $E_T(C = C)$ , is given by the sum of two times  $E_T(C = C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell due to the decrease in radius with the formation of the  $C = C$  -bond MO (Eq. (14.247)), and  $E_T(C = C, \sigma)$ , the  $\sigma$  MO  
10 contribution given by Eq. (14.422):

$$\begin{aligned} E_T(C = C) &= 2E_T(C = C, 2sp^3) + E_T(C = C, \sigma) \\ &= \left( 2(-1.13380 \text{ eV}) + \left( -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.85252) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \right) \right) \\ &= 2(-1.13380 \text{ eV}) + (-63.27074 \text{ eV}) = -65.53833 \text{ eV} \end{aligned} \quad (14.483)$$

which is the same  $E_T(C = C, \sigma)$  of ethylene given by Eq. (14.324).

## VIBRATION OF BENZENE

15 The  $C = C$  vibrational energy levels of  $C_6H_6$  may be solved as six sets of equivalent coupled harmonic oscillators where each  $C$  is a further coupled to the corresponding  $C - H$  oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of  
20 Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $C = C$ -BOND MO ELEMENT

## OF BENZENE

The equations of the radiation reaction force of the  $C = C$  -bond MO of benzene are given by Eq. (13.142), except the force-constant factor is  $(0.85252)0.5$  based on the force constant  $k'$  of Eq. (14.418), and the  $C = C$  -bond MO parameters are used. The angular frequency of the  
5 reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.85252(0.5)e^2}{4\pi\epsilon_0 b^3}} = 4.97272 \times 10^{16} \text{ rad/s} \quad (14.484)$$

where  $b$  is given by Eq. (14.428). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 4.97272 \times 10^{16} \text{ rad/s} = 32.73133 \text{ eV} \quad (14.485)$$

10 In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$  -type MO, for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (14.485) for  $\bar{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63536831 \text{ eV} \sqrt{\frac{2e(32.73133 \text{ eV})}{m_e c^2}} = -0.35806 \text{ eV} \quad (14.486)$$

15 In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the  $C = C$  -bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (14.486) and  $\bar{E}_{Kvib}$ , the average kinetic energy of  
20 vibration which is 1/2 of the vibrational energy of the  $C = C$  bond. Using the experimental  $C = C$   $E_{vib}(\nu_{16})$  of  $1584.8 \text{ cm}^{-1}$  ( $0.19649 \text{ eV}$ ) [16] for  $\bar{E}_{Kvib}$  of the transition state having two bonds,  $\bar{E}'_{osc}(C = C, \sigma)$  per bond is

$$\bar{E}'_{osc}(C = C, \sigma) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (14.487)$$

$$\bar{E}'_{osc}(C = C, \sigma) = -0.35806 \text{ eV} + \frac{1}{2} (0.19649 \text{ eV}) = -0.25982 \text{ eV} \quad (14.488)$$



Given that the vibration and reentrant oscillation is for two  $C-C$  bonds of each  $C=C$  double bond,  $\bar{E}_{benzene\ osc}(C=C, \sigma)$ , is:

$$\bar{E}_{benzene\ osc}(C=C, \sigma) = 2 \left( \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) = 2 \left( -0.35806\ eV + \frac{1}{2} (0.19649\ eV) \right) = -0.51963\ eV \quad (14.489)$$

5

### TOTAL ENERGIES OF THE $C=C$ -BOND MO ELEMENT OF BENZENE

$E_{T+osc}(C=C)$ , the total energy of the  $C=C$ -bond MO of benzene including the Doppler term, is given by the sum of  $E_T(C=C)$  (Eq. (14.483)) and  $\bar{E}_{benzene\ osc}(C=C, \sigma)$  given by Eq. (14.489):

$$\begin{aligned} E_{T+osc}(C=C) &= V_e + T + V_m + V_p + 2E_T(C=C, 2sp^3) + \bar{E}_{benzene\ osc}(C=C, \sigma) \\ 10 \quad &= E_T(C=C, \sigma) + 2E_T(C=C, 2sp^3) + \bar{E}_{benzene\ osc}(C=C, \sigma) \\ &= E_T(C=C) + \bar{E}_{benzene\ osc}(C=C, \sigma) \end{aligned} \quad (14.490)$$

$$E_{T+osc}(C=C) = \left\{ \left( \frac{-2e^2}{8\pi\epsilon_0 c'} \left[ (0.85252) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] + 2E_T(C=C, 2sp^3) \right) \right. \\ \left. - 2 \left( (31.63536831\ eV) \sqrt{\frac{2\hbar \sqrt{(0.85252) \frac{1}{2} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}} \right) \right\} \quad (14.491)$$

$$= -65.53833\ eV - 2 \left( 0.35806\ eV - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$

From Eqs. (14.489-14.491), the total energy of the  $C=C$ -bond MO is

$$\begin{aligned} E_{T+osc}(C=C) &= -63.27074\ eV + 2E_T(C=C, 2sp^3) + \bar{E}_{benzene\ osc}(C=C, \sigma) \\ &= -63.27074\ eV + 2(-1.13380\ eV) - 2 \left( 0.35806\ eV - \frac{1}{2} (0.19649\ eV) \right) \\ &= -66.05796\ eV \end{aligned} \quad (14.492)$$

15

where the experimental  $E_{vib}$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

## TOTAL BOND DISSOCIATION ENERGY OF BENZENE

Ethylene serves as a basis element for the  $C=C$  bonding of benzene wherein each of the six  $C=C$  bonds of benzene comprises  $(0.75)(4) = 3$  electrons according to Eq. (14.416). The

total energy of the bonds of the eighteen electrons of the  $C=C$  bonds of benzene,  $E_T(C_6H_6, C=C)$ , is given by  $(6)(0.75)$  times  $E_{T+osc}(C=C)$  (Eq. (14.492)), the total energy of the  $C=C$ -bond MO of benzene including the Doppler term, minus eighteen times  $E(C, 2sp^3)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each  $C$  that forms the double  $C=C$  bonds. Thus, the total energy of the six  $C=C$  bonds of benzene is

$$\begin{aligned} E_T(C_6H_6, C=C) &= (6)(0.75)E_{T+osc}(C=C) - 18E(C, 2sp^3) \\ &= (6)(0.75)(-66.05796 \text{ eV}) - 18(-14.63489 \text{ eV}) \\ &= -297.26081 \text{ eV} - (-263.42798 \text{ eV}) \\ &= -33.83284 \text{ eV} \end{aligned} \quad (14.493)$$

Each of the  $C-H$  bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each  $C-H$  bond,  $-E_{D_{benzene}}(^{12}CH)$  (Eq. (14.477)), the total energy of the twelve electrons of the six  $C-H$  bonds of benzene,  $E_T(C_6H_6, C-H)$ , is given by

$$E_T(C_6H_6, C-H) = (6)(-E_{D_{benzene}}(^{12}CH)) = 6(-3.90454 \text{ eV}) = -23.42724 \text{ eV} \quad (14.494)$$

The total bond dissociation energy of benzene,  $E_D(C_6H_6)$ , is given by the negative sum of

$E_T(C_6H_6, C=C)$  (Eq. (14.493)) and  $E_T(C_6H_6, C-H)$  (Eq. (14.494)):

$$\begin{aligned} E_D(C_6H_6) &= -\left(E_T(C_6H_6, C=C) + E_T(C_6H_6, C-H)\right) \\ &= -((-33.83284 \text{ eV}) + (-23.42724 \text{ eV})) \\ &= 57.2601 \text{ eV} \end{aligned} \quad (14.495)$$

The experimental total bond dissociation energy of benzene,  $E_T(C_6H_6)$ , is given by the negative difference between the enthalpy of its formation ( $\Delta H_f(\text{benzene}(\text{gas}))$ ) and the sum of the enthalpy of the formation of the gaseous carbons ( $\Delta H_f(C(\text{gas}))$ ) and hydrogen

( $\Delta H_f(H(\text{gas}))$ ) atoms. The heats of formation are [17-18]

$$\Delta H_f(\text{benzene}(\text{gas})) = 82.9 \text{ kJ/mole} \quad (0.8592 \text{ eV/molecule}) \quad (14.496)$$

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$$\Delta H_f(C(gas)) = 716.68 \text{ kJ/mole } (7.42774 \text{ eV/molecule}) \quad (14.497)$$

$$\Delta H_f(H(gas)) = 217.998 \text{ kJ/mole } (2.259353 \text{ eV/molecule}) \quad (14.498)$$

Thus, the total bond dissociation energy of benzene,  $E_D(C_6H_6)$ , is

$$\begin{aligned} E_D(C_6H_6) - E_T(C_6H_6) &= -(\Delta H_f(\text{benzene}(gas)) - (6\Delta H_f(C(gas)) + 6\Delta H_f(H(gas)))) \\ &= -(0.8592 \text{ eV} - 6(7.42774 \text{ eV} + 2.259353 \text{ eV})) \\ &= 57.26 \text{ eV} \end{aligned}$$

5 (14.499)

where  $E_T(C_6H_6)$  is the total energy of the bonds. The results of the determination of bond parameters of  $C_6H_6$  are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

10

### CONTINUOUS-CHAIN ALKANES ( $C_nH_{2n+2}$ , $n = 3, 4, 5 \dots \infty$ )

The continuous chain alkanes,  $C_nH_{2n+2}$ , are the homologous series comprising terminal methyl groups at each end of the chain with  $n-2$  methylene ( $CH_2$ ) groups in between:



15  $C_nH_{2n+2}$  can be solved using the same principles as those used to solve ethane and ethylene wherein the  $2s$  and  $2p$  shells of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Three  $H$  AOs combine with three carbon  $2sp^3$  HOs and two  $H$  AOs combine  
20 with two carbon  $2sp^3$  HOs to form each methyl and methylene group, respectively, where each bond comprises a  $H_2$ -type MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. The  $CH_3$  and  $CH_2$  groups bond by forming  $H_2$ -type MOs between the remaining  $C2sp^3$  HOs on the carbons such that each carbon forms four bonds involving its four  $C2sp^3$  HOs.

25

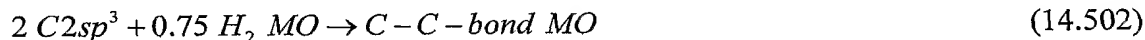
# FORCE BALANCE OF THE C – C -BOND MOs OF CONTINUOUS-CHAIN ALKANES

$C_nH_{2n+2}$  comprises a chemical bond between two terminal  $CH_3$  radicals and  $n-2$   $CH_2$  radicals wherein each methyl and methylene radical comprises three and two chemical bonds, respectively, between carbon and hydrogen atoms. The solution of the parameters of  $CH_3$  is given in the Methyl Radical ( $CH_3$ ) section. The solution of the parameters of  $CH_2$  is given in the Dihydrogen Carbide Radical ( $CH_2$ ) section and follows the same procedure. Each C – H bond having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75%  $H_2$ -type ellipsoidal MO and 25%  $C2sp^3$  HO as given by Eq. (13.429):



The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , each of the C – H-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that is continuous with the  $C2sp^3$  shell at the C atom whose nucleus serves as the other focus. The electron configuration and the energy,  $E(C, 2sp^3)$ , of the  $C2sp^3$  shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of each C – H bond is provided by the spin-pairing force of the  $CH_3$  or  $CH_2$  MO that has the symmetry of an s orbital that superimposes with the  $C2sp^3$  orbitals such that the corresponding angular momenta are unchanged. The energies of each  $CH_3$  and  $CH_2$  MO involve each  $C2sp^3$  and each  $H1s$  electron with the formation of each C – H bond. The sum of the energies of the  $H_2$ -type ellipsoidal MOs is matched to that of the  $C2sp^3$  shell. The force balance of the C – H-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.139) and the energy matching condition between the  $C2sp^3$ -HO components of the MO.

The  $CH_3$  and  $CH_2$  groups form  $C-C$  bonds comprising  $H_2$ -type MOs between the remaining  $C2sp^3$  HOs on the carbons such that each carbon forms four bonds involving its four  $C2sp^3$  HOs. The sharing of electrons between any two  $C2sp^3$  HOs to form a molecular orbital (MO) comprising two spin-paired electrons permits each  $C2sp^3$  HO to decrease in radius and energy. As in the case of the  $C-H$  bonds, each  $C-C$ -bond MO is a prolate-spheroidal-MO surface that cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the  $C2sp^3$  shell at each  $C$  atom. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the  $C2sp^3$  shell. As in the case of previous examples of energy-matched MOs such as the  $C-C$ -bond MO of ethane, each  $C-C$ -bond MO of  $C_nH_{2n+2}$  must comprise 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $C-C$ -bond MO must comprise two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the two  $C2sp^3$  HOs:



The linear combination of the  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution from each  $C2sp^3$  HO to the  $C-C$ -bond MO to achieve an energy minimum. The force balance of the  $C-C$ -bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.502) and the energy matching condition between the  $C2sp^3$ -HO components of the MO.

Before bonding, the  $2sp^3$  hybridized orbital arrangement of each carbon atom is given by Eq. (14.140). The sum  $E_T(C, 2sp^3)$  of calculated energies of  $C$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  is given by Eq. (14.141). The radius  $r_{2sp^3}$  of the  $C2sp^3$  shell is given by Eq. (14.142). The Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  and the energy  $E(C, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell are given by Eqs. (14.143) and (14.146), respectively.

The formation of each  $C-C$  bond of  $C_nH_{2n+2}$  further requires that the energy of all

$H_2$ -type prolate spheroidal MOs ( $\sigma$  MOs) be matched at all  $C2sp^3$  HOs since they are continuous throughout the molecule. Thus, the energy of each  $C2sp^3$  HO must be a linear combination of that of the  $CH_3$  and  $CH_2$  groups that serve as basis elements. Each  $CH_3$  forms one  $C-C$  bond, and each  $CH_2$  group forms two. Thus, the energy of each  $C2sp^3$  HO of each  $CH_3$  and  $CH_2$  group alone is given by that in ethane and ethylene, respectively. The parameters of ethane and ethylene are given by Eqs. (14.147-14.151) and (14.244-14.247), respectively. The alkane parameters can be determined by first reviewing those of ethane and ethylene.

With the formation of the  $C-C$ -bond MO of ethane from two methyl radicals, each having a  $C2sp^3$  electron with an energy given by Eq. (14.146), the total energy of the state is given by the sum over the four electrons. The sum  $E_T(C_{ethane}, 2sp^3)$  of calculated energies of  $C2sp^3$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  given by Eq. (14.147), is

$$\begin{aligned} E_T(C_{ethane}, 2sp^3) &= -(64.3921 \text{ eV} + 48.3125 \text{ eV} + 24.2762 \text{ eV} + E(C, 2sp^3)) \\ &= -(64.3921 \text{ eV} + 48.3125 \text{ eV} + 24.2762 \text{ eV} + 14.63489 \text{ eV}) \quad (14.503) \\ &= -151.61569 \text{ eV} \end{aligned}$$

where  $E(C, 2sp^3)$  is the sum of the energy of  $C$ ,  $-11.27671 \text{ eV}$ , and the hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the  $E_T(C_{ethane}, 2sp^3)$  is purely Coulombic.

The sharing of electrons between two  $C2sp^3$  HOs to form a  $C-C$ -bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each  $C2sp^3$  HO donates an excess of 25% of its electron density to the  $C-C$ -bond MO to form an energy minimum. By considering this electron redistribution in the ethane molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{ethane 2sp^3}$  of the  $C2sp^3$  shell of ethane may be calculated from the Coulombic energy using Eq.

(10.102):

$$r_{ethane 2sp^3} = \left( \sum_{n=2}^5 (Z-n) - 0.25 \right) \frac{e^2}{8\pi\epsilon_0 (e151.61569 \text{ eV})} = \frac{9.75e^2}{8\pi\epsilon_0 (e151.61569 \text{ eV})} = 0.87495a_0 \quad (14.504)$$

Using Eqs. (10.102) and (14.504), the Coulombic energy  $E_{Coulomb}(C_{ethane}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E_{Coulomb}(C_{ethane}, 2sp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{ethane 2sp^3}} = \frac{-e^2}{8\pi\epsilon_0 0.87495a_0} = -15.55033 \text{ eV} \quad (14.505)$$

During hybridization, one of the spin-paired  $2s$  electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (14.505), the energy  $E(C_{ethane}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E(C_{ethane}, 2sp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{ethane 2sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} = -15.55033 \text{ eV} + 0.19086 \text{ eV} = -15.35946 \text{ eV} \quad (14.506)$$

Thus,  $E_T(C-C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell with the formation of the  $C-C$ -bond MO is given by the difference between Eq. (14.146) and Eq. (14.506):

$$E_T(C-C, 2sp^3) = E(C_{ethane}, 2sp^3) - E(C, 2sp^3) = -15.35946 \text{ eV} - (-14.63489 \text{ eV}) = -0.72457 \text{ eV} \quad (14.507)$$

Next, consider the formation of the  $C=C$ -bond MO of ethylene from two  $CH_2$  radicals, each having a  $C2sp^3$  electron with an energy given by Eq. (14.146). The sum  $E_T(C_{ethylene}, 2sp^3)$  of calculated energies of  $C2sp^3$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  is given by Eq. (14.147). The sharing of electrons between two pairs of  $C2sp^3$  HOs to form a  $C=C$ -bond MO permits each participating HO to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating  $C2sp^3$  HO donates an excess of 25% of its electron density to the  $C=C$ -bond MO to form an energy minimum. By considering this electron redistribution in the ethylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{ethylene 2sp^3}$  of the  $C2sp^3$  shell of ethylene may be calculated from the Coulombic energy using Eqs. (10.102) and (14.147):

$$\begin{aligned}
 r_{ethylene 2sp^3} &= \left( \sum_{n=2}^5 (Z-n) - 0.5 \right) \frac{408 e^2}{8\pi\epsilon_0 (e151.61569 \text{ eV})} \\
 &= \frac{9.5e^2}{8\pi\epsilon_0 (e151.61569 \text{ eV})} \\
 &= 0.85252a_0
 \end{aligned} \tag{14.508}$$

where  $Z=6$  for carbon. Using Eqs. (10.102) and (14.508), the Coulombic energy  $E_{Coulomb}(C_{ethylene}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E_{Coulomb}(C_{ethylene}, 2sp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{ethylene 2sp^3}} = \frac{-e^2}{8\pi\epsilon_0 0.85252a_0} = -15.95955 \text{ eV} \tag{14.509}$$

5 During hybridization, one of the spin-paired  $2s$  electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (14.509), the energy  $E(C_{ethylene}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E(C_{ethylene}, 2sp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{ethylene 2sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} = -15.95955 \text{ eV} + 0.19086 \text{ eV} = -15.76868 \text{ eV} \tag{14.510}$$

Thus,  $E_T(C=C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell with the formation of the  $C=C$ -bond MO is given by the difference between Eq. (14.146) and Eq. (14.510):

$$\begin{aligned}
 E_T(C=C, 2sp^3) &= E(C_{ethylene}, 2sp^3) - E(C, 2sp^3) \\
 &= -15.76868 \text{ eV} - (-14.63489 \text{ eV}) \\
 &= -1.13380 \text{ eV}
 \end{aligned} \tag{14.511}$$

To meet the energy matching condition for all  $\sigma$  MOs at all  $C2sp^3$  HOs, the energy  $E(C_{alkane}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell of each alkane carbon atom must be the average of  $E(C_{ethane}, 2sp^3)$  (Eq. (14.506)) and  $E(C_{ethylene}, 2sp^3)$  (Eq. (14.510)):

$$\begin{aligned}
 E(C_{alkane}, 2sp^3) &= \frac{E(C_{ethane}, 2sp^3) + E(C_{ethylene}, 2sp^3)}{2} \\
 &= \frac{(-15.35946 \text{ eV}) + (-15.76868 \text{ eV})}{2} \\
 &= -15.56407 \text{ eV}
 \end{aligned} \tag{14.512}$$



And,  $E_{T_{alkane}}(C-C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell with the formation of each  $C-C$ -bond MO, must be the average of  $E_T(C-C, 2sp^3)$  (Eq. (14.507)) and  $E_T(C=C, 2sp^3)$  (Eq. (14.511)):

$$\begin{aligned} E_{T_{alkane}}(C-C, 2sp^3) &= \frac{E_T(C-C, 2sp^3) + E_T(C=C, 2sp^3)}{2} \\ &= \frac{(-0.72457 \text{ eV}) + (-1.13379 \text{ eV})}{2} \\ &= -0.92918 \text{ eV} \end{aligned} \quad (14.513)$$

- 5 Using Eq. (10.102), the radius  $r_{alkane2sp^3}$  of the  $C2sp^3$  shell of each carbon atom of  $C_nH_{2n+2}$  may be calculated from the Coulombic energy using the initial energy  $E_{Coulomb}(C, 2sp^3) = -14.82575 \text{ eV}$  (Eq. (14.143)) and  $E_{T_{alkane}}(C-C, 2sp^3)$  Eq. (14.513)), the energy change of each  $C2sp^3$  shell with the formation of each  $C-C$ -bond MO. Consider the case of a methyl carbon which donates  $E_{T_{alkane}}(C-C, 2sp^3)$  Eq. (14.513)) to a single
- 10  $C-C$  bond:

$$\begin{aligned} r_{alkane2sp^3} &= \frac{-e^2}{8\pi\epsilon_0(E_{Coulomb}(C, 2sp^3) + E_{T_{alkane}}(C-C, 2sp^3))} \\ &= \frac{e^2}{8\pi\epsilon_0(14.825751 \text{ eV} + 0.92918 \text{ eV})} \\ &= 0.86359a_0 \end{aligned} \quad (14.514)$$

Using Eqs. (10.102) and (14.514), the Coulombic energy  $E_{Coulomb}(C_{alkane}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$15 \quad E_{Coulomb}(C_{alkane}, 2sp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{alkane2sp^3}} = \frac{-e^2}{8\pi\epsilon_0 0.86359a_0} = -15.75493 \text{ eV} \quad (14.515)$$

During hybridization, one of the spin-paired  $2s$  electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (14.515), the energy  $E(C_{alkane}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$20 \quad E(C_{alkane}, 2sp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{alkane2sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} = -15.75493 \text{ eV} + 0.19086 \text{ eV} = -15.56407 \text{ eV}$$

(14.516)

Thus,  $E_{T_{alkane}}(C-C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell with the formation of each  $C-C$  bond MO is given by the difference between Eq. (14.146) and Eq. (14.516):

$$E_{T_{alkane}}(C-C, 2sp^3) = E(C_{alkane}, 2sp^3) - E(C, 2sp^3) = -15.56407 \text{ eV} - (-14.63489 \text{ eV}) = -0.92918 \text{ eV} \quad (14.517)$$

which agrees with Eq. (14.513).

The energy contribution due to the charge donation at each carbon superimposes linearly. In general, the radius  $r_{mol2sp^3}$  of the  $C2sp^3$  HO of a carbon atom of a group of a given molecule is calculated using Eq. (14.514) by considering  $\sum E_{T_{mol}}(MO, 2sp^3)$ , the total energy donation to each bond with which it participates in bonding. The general equation for the radius is given by

$$\begin{aligned} r_{mol2sp^3} &= \frac{-e^2}{8\pi\epsilon_0 \left( E_{Coulomb}(C, 2sp^3) + \sum E_{T_{mol}}(MO, 2sp^3) \right)} \\ &= \frac{e^2}{8\pi\epsilon_0 \left( e14.825751 \text{ eV} + \sum |E_{T_{mol}}(MO, 2sp^3)| \right)} \end{aligned} \quad (14.518)$$

The  $C2sp^3$  HO of each methyl group of an alkane contributes  $-0.92918 \text{ eV}$  to the corresponding single  $C-C$  bond; thus, the corresponding  $C2sp^3$  HO radius is given by Eq. (14.514). The  $C2sp^3$  HO of each methylene group of  $C_nH_{2n+2}$  contributes  $-0.92918 \text{ eV}$  to each of the two corresponding  $C-C$  bond MOs. Thus, the radius of each methylene group of an alkane is given by

$$\begin{aligned} r_{alkaneC_{methylene}2sp^3} &= \frac{-e^2}{8\pi\epsilon_0 \left( E_{Coulomb}(C, 2sp^3) + \sum E_{T_{alkane}}(methylene C-C, 2sp^3) \right)} \\ &= \frac{e^2}{8\pi\epsilon_0 (e14.825751 \text{ eV} + e0.92918 \text{ eV} + e0.92918 \text{ eV})} \\ &= 0.81549a_0 \end{aligned} \quad (14.519)$$

As in the case with ethane, the  $H_2$ -type ellipsoidal MO comprises 75% of the  $C-C$  bond MO shared between two  $C2sp^3$  HOs corresponding to the electron charge density in Eq. (11.65) of  $\frac{-0.75e}{2}$ . But, the additional 25% charge-density contribution to the  $C-C$  bond MO causes the electron charge density in Eq. (11.65) to be given by  $\frac{-e}{2} = -0.5e$ .

Thus, the force constant  $k'$  to determine the ellipsoidal parameter  $c'$  in terms of the central force of the foci is given by Eq. (14.152). The distance from the origin of the  $C-C$ -bond MO to each focus  $c'$  is given by Eq. (14.153). The internuclear distance from is given by Eq. (14.154). The length of the semiminor axis of the prolate spheroidal  $C-C$ -bond MO  $b = c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of the  $C-C$ -bond MO. Since the  $C-C$ -bond MO comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $C_{alkane}2sp^3$  HO of each carbon, the energy  $E(C_{alkane}, 2sp^3)$  in Eq. (14.512) adds to that of the  $H_2$ -type ellipsoidal MO to give the total energy of the  $C-C$ -bond MO. From the energy equation and the relationship between the axes, the dimensions of the  $C-C$ -bond MO are solved. Similarly,  $E(C_{alkane}, 2sp^3)$  is added to the energy of the  $H_2$ -type ellipsoidal MO of each  $C-H$  bond of the methyl and methylene groups to give their total energy. From the energy equation and the relationship between the axes, the dimensions of the equivalent  $C-H$ -bond MOs of the methyl and methylene groups in the alkane are solved.

The general equations for the energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  of each  $C-C$ -bond MO are the same as those of the  $CH$  MO except that energy of the  $C_{alkane}2sp^3$  HO is used. The energy components at each carbon atom superimpose linearly and may be treated independently. Since each prolate spheroidal  $H_2$ -type MO transitions to the  $C_{alkane}2sp^3$  HO of each corresponding carbon of the bond and the energy of the  $C_{alkane}2sp^3$  shell treated independently must remain constant and equal to the  $E(C_{alkane}, 2sp^3)$  given by Eq. (14.512), the total energy  $E'_{T_{alkane}}(C-C, \sigma)$  of the  $\sigma$  component of each  $C-C$ -bond MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C_{alkane}2sp^3$  HO and the  $H_2$ -type ellipsoidal MO that forms the  $\sigma$  component of the  $C-C$ -bond MO as given by Eq. (14.502) with the electron charge redistribution. The total number of  $C-C$  bonds in  $C_nH_{2n+2}$  is  $n-1$ . Using Eqs. (13.431) and (14.512),  $E'_{T_{alkane}}(C-C, \sigma)$  of the  $n-1$  bonds is given by

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$$E_{T_{alkane}}(C-C, \sigma) = (n-1) \left( E_T + E(C_{alkane}, 2sp^3) \right) \\ = (n-1) \left( -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 \text{ eV} \right) \quad (14.520)$$

To match the boundary condition that the total energy of each  $H_2$ -type ellipsoidal MO is given by Eqs. (11.212) and (13.75),  $E_{T_{alkane}}(C-C, \sigma)$  given by Eq. (14.520) is set equal to  $(n-1)$  times Eq. (13.75):

$$E_{T_{alkane}}(C-C, \sigma) = \\ 5 \quad (n-1) \left( -\frac{e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 \text{ eV} \right) = (n-1)(-31.63536831 \text{ eV}) \quad (14.521)$$

From the energy relationship given by Eq. (14.521) and the relationship between the axes given by Eqs. (14.153-14.154) and (13.62-13.63), the dimensions of the  $C-C$ -bond MO can be solved.

10 Substitution of Eq. (14.153) into Eq. (14.521) gives

$$\frac{e^2}{8\pi\epsilon_0 \sqrt{aa_0}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}} - 1 \right] = e16.07130 \quad (14.522)$$

The most convenient way to solve Eq. (14.522) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 2.12499a_0 = 1.12450 \times 10^{-10} \text{ m} \quad (14.523)$$

15 Substitution of Eq. (14.523) into Eq. (14.155) gives

$$c' = 1.45774a_0 = 7.71400 \times 10^{-11} \text{ m} \quad (14.524)$$

The internuclear distance given by multiplying Eq. (14.524) by two is

$$2c' = 2.91547a_0 = 1.54280 \times 10^{-10} \text{ m} \quad (14.525)$$

The experimental  $C-C$  bond distance of propane is [3]

$$20 \quad 2c' = 1.532 \times 10^{-10} \text{ m} \quad (14.526)$$

The experimental  $C-C$  bond distance of butane is [3]

$$2c' = 1.531 \times 10^{-10} \text{ m} \quad (14.527)$$

Substitution of Eqs. (14.523-14.524) into Eq. (13.62) gives

$$b = c = 1.54616a_0 = 8.18192 \times 10^{-11} \text{ m} \quad (14.528)$$

25 Substitution of Eqs. (14.523-14.524) into Eq. (13.63) gives

$$e = 0.68600 \quad (14.529)$$

The nucleus of the  $C$  atoms comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{alkane} 2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is  
 5 given by Eq. (13.261) where for methylene bonds  $r_n = r_{alkane 2sp^3} = r_{methylene 2sp^3} = 0.81549a_0$  is the radius of the  $C_{alkane} 2sp^3$  shell given by Eq. (14.519). Substitution of Eqs. (14.523-14.524) into Eq. (13.261) gives

$$\theta' = 56.41^\circ \quad (14.530)$$

Then, the angle  $\theta_{C-C_{alkane} 2sp^3 HO}$  the radial vector of the  $C 2sp^3$  HO makes with the internuclear  
 10 axis is

$$\theta_{C-C_{alkane} 2sp^3 HO} = 180^\circ - 56.41^\circ = 123.59^\circ \quad (14.531)$$

as shown in Figure 48.

15 Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-C_{alkane}, H_2 MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{alkane} 2sp^3$  radial vector obeys the following relationship:

$$r_{alkane 2sp^3} \sin \theta_{C-C_{alkane} 2sp^3 HO} = 0.81549a_0 \sin \theta_{C-C_{alkane} 2sp^3 HO} = b \sin \theta_{C-C_{alkane}, H_2 MO} \quad (14.532)$$

20 such that

$$\theta_{C-C_{alkane}, H_2 MO} = \sin^{-1} \frac{0.81549a_0 \sin \theta_{C-C_{alkane} 2sp^3 HO}}{b} = \sin^{-1} \frac{0.81549a_0 \sin 123.59^\circ}{b} \quad (14.533)$$

with the use of Eq. (14.531). Substitution of Eq. (14.528) into Eq. (14.533) gives

$$\theta_{C-C_{alkane}, H_2 MO} = 26.06^\circ \quad (14.534)$$

Then, the distance  $d_{C-C_{alkane}, H_2 MO}$  along the internuclear axis from the origin of  $H_2$ -type  
 25 ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-C_{alkane}, H_2 MO} = a \cos \theta_{C-C_{alkane}, H_2 MO} \quad (14.535)$$

Substitution of Eqs. (14.523) and (14.534) into Eq. (14.535) gives

$$d_{C-C_{alkane}, H_2 MO} = 1.90890a_0 = 1.01015 \times 10^{-10} \text{ m} \quad (14.536)$$

The distance  $d_{C-C_{alkane} 2sp^3 HO}$  along the internuclear axis from the origin of the  $C$  atom to the point of intersection of the orbitals is given by

$$d_{C-C_{alkane} 2sp^3 HO} = d_{C-C_{alkane}, H_2 MO} - c' \quad (14.537)$$

Substitution of Eqs. (14.524) and (14.536) into Eq. (14.537) gives

$$5 \quad d_{C-C_{alkane} 2sp^3 HO} = 0.45117a_0 = 2.38748 \times 10^{-11} m \quad (14.538)$$

## FORCE BALANCE OF THE $CH_3$ MOs OF CONTINUOUS-CHAIN ALKANES

Each of the two  $CH_3$  MOs must comprise three equivalent  $C-H$  bonds with each  
10 comprising 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO as given by Eq. (13.540):

$$3[1 C2sp^3 + 0.75 H_2 MO] \rightarrow CH_3 MO \quad (14.539)$$

The force balance of the  $CH_3$  MO is determined by the boundary conditions that arise from  
15 the linear combination of orbitals according to Eq. (14.539) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant  $k'$  to determine the ellipsoidal parameter  $c'$  of the each  $H_2$ -type-ellipsoidal-MO component of the  $CH_3$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each  $C-H$ -bond MO to each focus  $c'$  is  
20 given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal  $C-H$ -bond MO  $b = c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of each  $C-H$ -bond MO. Since each of the three prolate spheroidal  $C-H$ -bond MOs comprises an  $H_2$ -type-  
25 ellipsoidal MO that transitions to the  $C_{alkane} 2sp^3$  HO of  $C_n H_{2n+2}$ , the energy  $E(C_{alkane}, 2sp^3)$  of Eq. (14.512) adds to that of the three corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $CH_3$  MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH_3$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ ,  $T$ , and  $V_m$  are the same as those of methyl radical, three times those of  $CH$  corresponding to the three  $C-H$  bonds except that energy of the  $C_{alkane} 2sp^3$  HO is used. Since the each prolate spheroidal  $H_2$ -type MO transitions to the  $C_{alkane} 2sp^3$  HO and the energy of the  $C_{alkane} 2sp^3$  shell must remain constant and equal to the  $E(C_{alkane}, 2sp^3)$  given by Eq. (14.512), the total energy  $E_{T_{alkane}}(CH_3)$  of the  $CH_3$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C_{alkane} 2sp^3$  HO and the three  $H_2$ -type ellipsoidal MOs that forms the  $CH_3$  MO as given by Eq. (14.539). Using Eq. (13.431) or Eq. (13.541),  $E_{T_{alkane}}(CH_3)$  is given by

$$E_{T_{alkane}}(CH_3) = E_T + E(C_{alkane}, 2sp^3) \\ = -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 \text{ eV} \quad (14.540)$$

$E_{T_{alkane}}(CH_3)$  given by Eq. (14.540) is set equal to three times the energy of the  $H_2$ -type ellipsoidal MO minus two times the Coulombic energy of  $H$  given by Eq. (13.542):

$$E_T(CH_3) = -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 \text{ eV} = -67.69450 \text{ eV} \quad (14.541)$$

From the energy relationship given by Eq. (14.541) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH_3$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.541) gives

$$\frac{3e^2}{8\pi\epsilon_0 \sqrt{\frac{2aa_0}{3}}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right] = e52.13044 \quad (14.542)$$

The most convenient way to solve Eq. (14.542) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.64920a_0 = 8.72720 \times 10^{-11} \text{ m} \quad (14.543)$$

Substitution of Eq. (14.543) into Eq. (14.60) gives

$$c' = 1.04856a_0 = 5.54872 \times 10^{-11} \text{ m} \quad (14.544)$$

The internuclear distance given by multiplying Eq. (14.544) by two is

$$2c' = 2.09711a_0 = 1.10974 \times 10^{-10} \text{ m} \quad (14.545)$$

The experimental  $C-H$  bond distance of propane is [3]

$$2c' = 1.107 \times 10^{-10} \text{ m} \quad (14.546)$$

Substitution of Eqs. (14.543-14.544) into Eq. (14.62) gives

$$b = c = 1.27295a_0 = 6.73616 \times 10^{-11} \text{ m} \quad (14.547)$$

5 Substitution of Eqs. (14.543-14.544) into Eq. (14.63) gives

$$e = 0.63580 \quad (14.548)$$

The nucleus of the  $H$  atom and the nucleus of the  $C$  atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{alkane} 2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270).

10 The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{alkane 2sp^3} = 0.86359a_0$  is the radius of the  $C_{alkane} 2sp^3$  shell. Substitution of Eqs. (14.543-14.544) into Eq. (13.261) gives

$$\theta' = 77.49^\circ \quad (14.549)$$

Then, the angle  $\theta_{C-H_{alkane} 2sp^3 HO}$  the radial vector of the  $C 2sp^3$  HO makes with the internuclear

15 axis is

$$\theta_{C-H_{alkane} 2sp^3 HO} = 180^\circ - 77.49^\circ = 102.51^\circ \quad (14.550)$$

as shown in Figure 49.

20 The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-H_{alkane}, H_2 MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{alkane} 2sp^3$  radial vector obeys the following relationship:

$$r_{alkane 2sp^3} \sin \theta_{C-H_{alkane} 2sp^3 HO} = 0.86359a_0 \sin \theta_{C-H_{alkane} 2sp^3 HO} = b \sin \theta_{C-H_{alkane}, H_2 MO} \quad (14.551)$$

25 such that

$$\theta_{C-H_{alkane}, H_2 MO} = \sin^{-1} \frac{0.86359a_0 \sin \theta_{C-H_{alkane} 2sp^3 HO}}{b} = \sin^{-1} \frac{0.86359a_0 \sin 102.51^\circ}{b} \quad (14.552)$$

with the use of Eq. (14.550). Substitution of Eq. (14.547) into Eq. (14.552) gives

$$\theta_{C-H_{alkane}, H_2 MO} = 41.48^\circ \quad (14.553)$$



Then, the distance  $d_{C-H_{alkane}, H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{alkane}, H_2MO} = a \cos \theta_{C-H_{alkane}, H_2MO} \quad (14.554)$$

Substitution of Eqs. (14.543) and (14.553) into Eq. (14.554) gives

$$5 \quad d_{C-H_{alkane}, H_2MO} = 1.23564a_0 = 6.53871 \times 10^{-11} \text{ m} \quad (14.555)$$

The distance  $d_{C-H_{alkane} 2sp^3 HO}$  along the internuclear axis from the origin of the  $C$  atom to the point of intersection of the orbitals is given by

$$d_{C-H_{alkane} 2sp^3 HO} = d_{C-H_{alkane}, H_2MO} - c' \quad (14.556)$$

Substitution of Eqs. (14.544) and (14.555) into Eq. (14.556) gives

$$10 \quad d_{C-H_{alkane} 2sp^3 HO} = 0.18708a_0 = 9.89999 \times 10^{-12} \text{ m} \quad (14.557)$$

### BOND ANGLE OF THE $CH_3$ AND $CH_2$ GROUPS

Each  $CH_3$  MO comprises a linear combination of three  $C-H$ -bond MOs. Each  $C-H$ -bond MO comprises the superposition of a  $H_2$ -type ellipsoidal MO and the  $C_{alkane} 2sp^3$  HO.

- 15 A bond is also possible between the two H atoms of the  $C-H$  bonds. Such  $H-H$  bonding would decrease the  $C-H$  bond strength since electron density would be shifted from the  $C-H$  bonds to the  $H-H$  bond. Thus, the bond angle between the two  $C-H$  bonds is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal  $H$  atoms of the  $C-H$  bonds is zero. From Eqs. (11.79) and (13.228), the distance
- 20 from the origin to each focus of the  $H-H$  ellipsoidal MO is

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \quad (14.558)$$

The internuclear distance from Eq. (14.558) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \quad (14.559)$$

- The length of the semiminor axis of the prolate spheroidal  $H-H$  MO  $b = c$  is given by Eq.
- 25 (14.62).

The bond angle of the  $CH_3$  groups of  $C_n H_{2n+2}$  is derived by using the orbital composition and an energy matching factor as in the case with the  $CH_3$  radical. Since each pair of  $H_2$ -type ellipsoidal MOs initially comprise 75% of the  $H$  electron density of  $H_2$  and

the energy of each  $H_2$ -type ellipsoidal MO is matched to that of the  $C_{alkane}2sp^3$  HO, the component energies and the total energy  $E_T$  of the  $H-H$  bond are given by Eqs. (13.67-13.73) except that  $V_e$ ,  $T$ , and  $V_m$  are corrected for the hybridization-energy-matching factor of 0.86359. Hybridization with 25% electron donation to the  $C-C$ -bond gives rise to the

5  $C_{alkane}2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(C_{alkane}, 2sp^3)$  given by Eq. (14.515). The corresponding normalization factor for determining the zero of the total  $H-H$  bond energy is given by the ratio of 15.75493 eV, the magnitude of  $E_{Coulomb}(C_{alkane}, 2sp^3)$  given by Eq. (14.515), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). The hybridization energy factor  $C_{alkaneC2sp^3HO}$  is

$$10 \quad C_{alkaneC2sp^3HO} = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{alkane2sp^3}}} = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 0.86359 a_0}} = \frac{13.605804 \text{ eV}}{15.75493 \text{ eV}} = 0.86359 \quad (14.560)$$

Substitution of Eq. (14.558) into Eq. (13.233) with the hybridization factor of 0.86359 gives

$$(14.561) \quad 0 = \left[ \frac{-e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2}}} \left[ (0.86359)^{-1} \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 a^3}}}}{m_e c^2} \right] \right. \\ \left. + \hbar \sqrt{\frac{\frac{0.75e^2}{8\pi\epsilon_0 a^3} - \frac{e^2}{8\pi\epsilon_0 (a+c')^3}}{0.5m_p}} \right]$$

15 From the energy relationship given by Eq. (14.561) and the relationship between the axes given by Eqs. (14.558-14.559) and (14.62-14.63), the dimensions of the  $H-H$  MO can be solved.

The most convenient way to solve Eq. (14.561) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$20 \quad a = 5.8660a_0 = 3.1042 \times 10^{-10} \text{ m} \quad (14.562)$$

Substitution of Eq. (14.562) into Eq. (14.558) gives

$$c' = 1.7126a_0 = 9.0627 \times 10^{-11} \text{ m} \quad (14.563)$$

The internuclear distance given by multiplying Eq. (14.563) by two is

$$2c' = 3.4252a_0 = 1.8125 \times 10^{-10} \text{ m} \quad (14.564)$$

Substitution of Eqs. (14.562-14.563) into Eq. (14.62) gives

$$b = c = 5.6104a_0 = 2.9689 \times 10^{-10} \text{ m} \quad (14.565)$$

5 Substitution of Eqs. (14.562-14.563) into Eq. (14.63) gives

$$e = 0.2920 \quad (14.566)$$

Using  $2c'_{H-H}$  (Eq. (14.564)), the distance between the two  $H$  atoms when the total energy of the corresponding MO is zero (Eq. (14.561)), and  $2c'_{C-H}$ , the internuclear distance of each  $C-H$  bond, the corresponding bond angle can be determined from the law of  
10 cosines. Since the internuclear distance of each  $C-H$  bond of  $CH_3$  (Eq. (14.545)) and  $CH_2$  (Eq. (14.597)) are sufficiently equivalent, the bond angle determined with either is within experimental error of being the same. Using, Eqs. (13.242), (14.545), and (14.564), the bond angle  $\theta$  between the  $C-H$  bonds is

$$\theta = \cos^{-1} \left( \frac{2(2.09711)^2 - (3.4252)^2}{2(2.09711)^2} \right) = \cos^{-1}(-0.33383) = 109.50^\circ \quad (14.567)$$

15 The experimental angle between the  $C-H$  bonds is [19]

$$\theta = 109.3^\circ \quad (14.568)$$

The  $CH_3$  radical has a pyramidal structure with the carbon atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. The distance  $d_{origin-H}$  from the origin to the nucleus of a hydrogen atom given by Eqs. (14.564) and (13.412) is

$$20 \quad d_{origin-H} = 1.97754a_0 \quad (14.569)$$

The height along the z-axis of the pyramid from the origin to  $C$  nucleus  $d_{height}$  given by Eqs. (13.414), (14.545), and (14.569) is

$$d_{height} = 0.69800a_0 \quad (14.570)$$

The angle  $\theta_v$  of each  $C-H$  bond from the z-axis given by Eqs. (13.416), (14.569), and

25 (14.570) is

$$\theta_v = 70.56^\circ \quad (14.571)$$

The  $C-C$  bond is along the z-axis. Thus, the bond angle  $\theta_{C-C-H}$  between the internuclear axis of the  $C-C$  bond and a  $H$  atom of the methyl groups is given by

$$\theta_{C-C-H} = 180 - \theta_v \quad (14.572)$$

420

Substitution of Eq. (14.571) into Eq. (14.572) gives

$$\theta_{C-C-H} = 109.44^\circ \quad (14.573)$$

The experimental angle between the  $C-C-H$  bonds is [19]

$$\theta_{C-C-H} = 109.3^\circ \quad (14.574)$$

- 5 The  $C_nH_{2n+2}$  MOs shown in Figures 50-60 were rendered using these parameters. A minimum energy is obtained with a staggered configuration consistent with observations [3].

### ENERGIES OF THE $CH_3$ GROUPS

The energies of each  $CH_3$  group of  $C_nH_{2n+2}$  are given by the substitution of the  
10 semiprincipal axes (Eqs. (14.543-14.544) and (14.547)) into the energy equations of methyl radical (Eqs. (13.556-13.560)), with the exception that  $E(C_{alkane}, 2sp^3)$  (Eq. (14.514)) replaces  $E(C, 2sp^3)$  in Eq. (13.560):

$$V_e = 3(0.91771) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -107.32728 \text{ eV} \quad (14.575)$$

$$V_p = \frac{3e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 38.92728 \text{ eV} \quad (14.576)$$

$$15 \quad T = 3(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 32.53914 \text{ eV} \quad (14.577)$$

$$V_m = 3(0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.26957 \text{ eV} \quad (14.578)$$

$$E_{T_{alkane}}(CH_3) = \left( \begin{array}{l} -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \\ -15.56407 \text{ eV} \end{array} \right) = -67.69451 \text{ eV} \quad (14.579)$$

where  $E_{T_{alkane}}(CH_3)$  is given by Eq. (14.540) which is reiteratively matched to Eq. (13.542) within five-significant-figure round off error.

20

### VIBRATION OF THE $^{12}CH_3$ GROUPS

The vibrational energy levels of the  $C-H$  bonds of  $CH_3$  in  $C_nH_{2n+2}$  may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived

from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

### THE DOPPLER ENERGY TERMS OF THE $^{12}\text{CH}_3$ GROUPS

- 5 The equations of the radiation reaction force of the methyl groups in  $C_nH_{2n+2}$  are the same as those of the methyl radical with the substitution of the methyl-group parameters. Using Eq. (13.561), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 2.49286 \times 10^{16} \text{ rad/s} \quad (14.580)$$

- where  $b$  is given by Eq. (14.547). The kinetic energy,  $E_K$ , is given by Planck's equation  
10 (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.49286 \times 10^{16} \text{ rad/s} = 16.40846 \text{ eV} \quad (14.581)$$

- In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (14.581) for  $\bar{E}_K$  gives the Doppler energy of the electrons of each of the  
15 three bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(16.40846 \text{ eV})}{m_e c^2}} = -0.25352 \text{ eV} \quad (14.582)$$

- In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $\text{CH}_3$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic  
20 oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (14.582) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of each  $C-H$  bond. Using  $\omega_e$  given by Eq. (13.458) for  $\bar{E}_{Kvib}$  of the transition state having three independent bonds,  $\bar{E}'_{alkane\ osc} (^{12}\text{CH}_3)$  per bond is

$$\bar{E}'_{alkane\ osc} (^{12}\text{CH}_3) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (14.583)$$

- 25  $\bar{E}'_{alkane\ osc} (^{12}\text{CH}_3) = -0.25352 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) = -0.07586 \text{ eV} \quad (14.584)$

Given that the vibration and reentrant oscillation is for three  $C-H$  bonds,  $\bar{E}_{alkane\ osc} (^{12}CH_3)$ , is:

$$\begin{aligned}\bar{E}_{alkane\ osc} (^{12}CH_3) &= 3 \left( \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \\ &= 3 \left( -0.25352\ eV + \frac{1}{2} (0.35532\ eV) \right) \\ &= -0.22757\ eV\end{aligned}\quad (14.585)$$

## 5 TOTAL BOND ENERGIES OF THE $^{12}CH_3$ GROUPS

$E_{alkaneT+osc} (^{12}CH_3)$ , the total energy of each  $^{12}CH_3$  group including the Doppler term, is given by the sum of  $E_{T_{alkane}} (CH_3)$  (Eq. (14.579)) and  $\bar{E}_{alkane\ osc} (^{12}CH_3)$  given by Eq. (14.585):

$$\begin{aligned}E_{alkaneT+osc} (CH_3) &= V_e + T + V_m + V_p + E(C_{alkane}, 2sp^3) + \bar{E}_{alkane\ osc} (^{12}CH_3) \\ &= E_{T_{alkane}} (CH_3) + \bar{E}_{alkane\ osc} (^{12}CH_3)\end{aligned}\quad (14.586)$$

$$\begin{aligned}E_{alkaneT+osc} (^{12}CH_3) &= \left\{ \left( \frac{-3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407\ eV \right) \right. \\ &\quad \left. - 3 \left( (31.63536831\ eV) \sqrt{\frac{2\hbar \sqrt{\frac{3}{4} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}} \right) \right\} \\ &= -67.69450\ eV - 3 \left( 0.25352\ eV - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)\end{aligned}\quad (14.587)$$

From Eqs. (14.585-14.587), the total energy of each  $^{12}CH_3$  is

$$\begin{aligned}E_{alkaneT+osc} (^{12}CH_3) &= -67.69450\ eV + \bar{E}_{alkane\ osc} (^{12}CH_3) \\ &= -67.69450\ eV - 3 \left( 0.25352\ eV - \frac{1}{2} (0.35532\ eV) \right) \\ &= -67.92207\ eV\end{aligned}\quad (14.588)$$

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

The total  $CH_3$  bond dissociation energy,  $E_{D_{alkane}}(^{12}CH_3)$  is given by the sum of the initial  $C2sp^3$  HO energy,  $E(C, 2sp^3)$  (Eq. (14.146)), and three times the energy of the hydrogen atom,  $E_D(H)$  (Eq. (13.154)), minus  $E_{alkaneT+osc}(^{12}CH_3)$  (Eq. (14.588)):

$$E_{D_{alkane}}(^{12}CH_3) = E(C, 2sp^3) + 3E(H) - E_{alkaneT+osc}(^{12}CH_3) \quad (14.589)$$

5 Thus, the total  $^{12}CH_3$  bond dissociation energy,  $E_{D_{alkane}}(^{12}CH_3)$  is

$$\begin{aligned} E_{D_{alkane}}(^{12}CH_3) &= -(14.63489 \text{ eV} + 3(13.59844 \text{ eV})) - (E_{alkaneT+osc}(^{12}CH_2)) \\ &= -55.43021 \text{ eV} - (-67.92207 \text{ eV}) \\ &= 12.49186 \text{ eV} \end{aligned} \quad (14.590)$$

## FORCE BALANCE OF THE $CH_2$ MOs OF CONTINUOUS-CHAIN ALKANES

10 Each of the  $CH_2$  MOs must comprise two equivalent  $C-H$  bonds with each comprising 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO as given by Eq. (13.494):

$$2[1 C2sp^3 + 0.75 H_2 MO] \rightarrow CH_2 MO \quad (14.591)$$

15 The force balance of each  $CH_2$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.591) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant  $k'$  to determine the ellipsoidal parameter  $c'$  of the each  $H_2$ -type-ellipsoidal-MO component of the  $CH_2$  MO in terms of the central force of the foci is given  
20 by Eq. (13.59). The distance from the origin of each  $C-H$ -bond MO to each focus  $c'$  is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal  $C-H$ -bond MO  $b = c$  is given by Eq. (13.62). The eccentricity,  $e$ , is given by Eq. (13.63). The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of each  $C-H$ -bond  
25 MO. Since each of the two prolate spheroidal  $C-H$ -bond MOs comprises an  $H_2$ -type-ellipsoidal MO that transitions to the  $C_{alkane} 2sp^3$  HO of  $C_n H_{2n+2}$ , the energy  $E(C_{alkane}, 2sp^3)$

of Eq. (14.512) adds to that of the two corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $CH_2$  MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH_2$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ ,  $T$ , and  $V_m$  are the same as those of dihydrogen carbide radical, two times those of  $CH$  corresponding to the two  $C-H$  bonds except that energy of the  $C_{alkane} 2sp^3$  HO is used. Since the each prolate spheroidal  $H_2$ -type MO transitions to the  $C_{alkane} 2sp^3$  HO and the energy of the  $C_{alkane} 2sp^3$  shell treated independently must remain constant and equal to the  $E(C_{alkane}, 2sp^3)$  given by Eq. (14.512), the total energy  $E_{T_{alkane}}(CH_2)$  of the  $CH_2$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C_{alkane} 2sp^3$  HO and the two  $H_2$ -type ellipsoidal MOs that forms the  $CH_2$  MO as given by Eq. (14.591). Using Eq. (13.431) or Eq. (13.495),  $E_{T_{alkane}}(CH_2)$  is given by

$$\begin{aligned} E_{T_{alkane}}(CH_2) &= E_T + E(C_{alkane}, 2sp^3) \\ &= -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 \text{ eV} \end{aligned} \quad (14.592)$$

$E_{T_{alkane}}(CH_2)$  given by Eq. (14.592) is set equal to two times the energy of the  $H_2$ -type ellipsoidal MO minus the Coulombic energy of  $H$  given by Eq. (13.496):

$$E_T(CH_2) = -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 \text{ eV} = -49.66493 \text{ eV} \quad (14.593)$$

From the energy relationship given by Eq. (14.593) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH_2$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.593) gives

$$\frac{2e^2}{8\pi\epsilon_0 \sqrt{\frac{2aa_0}{3}}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right] = e34.10086 \quad (14.594)$$

The most convenient way to solve Eq. (14.594) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.67122a_0 = 8.84370 \times 10^{-11} \text{ m} \quad (14.595)$$



Substitution of Eq. (14.595) into Eq. (14.60) gives

$$c' = 1.05553a_0 = 5.58563 \times 10^{-11} \text{ m} \quad (14.596)$$

The internuclear distance given by multiplying Eq. (14.596) by two is

$$2c' = 2.11106a_0 = 1.11713 \times 10^{-10} \text{ m} \quad (14.597)$$

5 The experimental  $C-H$  bond distance of butane is [3]

$$2c' = 1.117 \times 10^{-10} \text{ m} \quad (14.598)$$

Substitution of Eqs. (14.595-14.596) into Eq. (14.62) gives

$$b = c = 1.29569a_0 = 6.85652 \times 10^{-11} \text{ m} \quad (14.599)$$

Substitution of Eqs. (14.595-14.596) into Eq. (14.63) gives

$$10 \quad e = 0.63159 \quad (14.600)$$

The nucleus of the  $H$  atom and the nucleus of the  $C$  atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{alkane}2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{methylene2sp^3} = 0.81549a_0$  is

15 the radius of the  $C_{methylene}2sp^3$  shell (Eq. (14.521)). Substitution of Eqs. (14.595-14.596) into Eq. (13.261) gives

$$\theta' = 68.47^\circ \quad (14.601)$$

Then, the angle  $\theta_{C-H_{alkane}2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$20 \quad \theta_{C-H_{alkane}2sp^3HO} = 180^\circ - 68.47^\circ = 111.53^\circ \quad (14.602)$$

as shown in Figure 49. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-H_{alkane},H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{alkane}2sp^3$  radial vector obeys the following relationship:

$$25 \quad r_{alkane2sp^3} \sin \theta_{C-H_{alkane}2sp^3HO} = 0.81549a_0 \sin \theta_{C-H_{alkane}2sp^3HO} = b \sin \theta_{C-H_{alkane},H_2MO} \quad (14.603)$$

such that

$$\theta_{C-H_{alkane},H_2MO} = \sin^{-1} \frac{0.81549a_0 \sin \theta_{C-H_{alkane}2sp^3HO}}{b} = \sin^{-1} \frac{0.81549a_0 \sin 111.53^\circ}{b} \quad (14.604)$$

with the use of Eq. (14.602). Substitution of Eq. (14.599) into Eq. (14.604) gives

$$\theta_{C-H_{alkane},H_2MO} = 35.84^\circ \quad (14.605)$$

Then, the distance  $d_{C-H_{alkane}, H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{alkane}, H_2MO} = a \cos \theta_{C-H_{alkane}, H_2MO} \quad (14.606)$$

Substitution of Eqs. (14.595) and (14.605) into Eq. (14.606) gives

$$5 \quad d_{C-H_{alkane}, H_2MO} = 1.35486a_0 = 7.16963 \times 10^{-11} \text{ m} \quad (14.607)$$

The distance  $d_{C-H_{alkane} 2sp^3 HO}$  along the internuclear axis from the origin of the  $C$  atom to the point of intersection of the orbitals is given by

$$d_{C-H_{alkane} 2sp^3 HO} = d_{C-H_{alkane}, H_2MO} - c' \quad (14.608)$$

Substitution of Eqs. (14.596) and (14.605) into Eq. (14.608) gives

$$10 \quad d_{C-H_{alkane} 2sp^3 HO} = 0.29933a_0 = 1.58400 \times 10^{-11} \text{ m} \quad (14.609)$$

The charge-density in each  $C-C$ -bond MO is increased by a factor of 0.25 with the formation of the  $C_{alkane} 2sp^3$  HOs each having a smaller radius. Using the orbital composition of the  $C-C$ -bond MOs (Eq. (14.504),  $CH_3$  groups (Eq. (14.539)), and the  $CH_2$  groups (Eq. (14.591)), the radii of  $C1s = 0.17113a_0$  (Eq. (10.51)),  $C_{alkane} 2sp^3 = 0.86359a_0$  (Eq. (14.514)),  
 15 and  $C_{alkane} 2sp^3 = C_{methylene} 2sp^3 = 0.81549a_0$  (Eq. (14.521)) shells, the parameters of the  $C-C$ -bonds (Eqs. (13.3-13.4), (14.523-14.525), and (14.528-14.538)), the parameters of the  $C-H$ -bond MOs of the  $CH_3$  groups (Eqs. (13.3-13.4), (14.544-14.545), and (14.547-14.557)), the parameters of the  $C-H$ -bond MOs of the  $CH_2$  groups (Eqs. (13.3-13.4), (14.595-14.597), and (14.599-14.609)), and the bond-angle parameters (Eqs. (14.562-  
 20 14.574)), the charge-density of the  $C_nH_{2n+2}$  MO comprising the linear combination  $2n+2$   $C-H$ -bond MOs and  $n-1$   $C-C$ -bond MOs, each bridging one or more methyl or methylene groups is shown for representative cases where data was available [17-18]. Propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and octadecane are shown in Figures 50-60, respectively. Each  $C-H$ -bond MO comprises a  
 25  $H_2$ -type ellipsoidal MO and a  $C_{alkane} 2sp^3$  HO having the dimensional diagram shown in Figure 48. Each  $C-C$ -bond MO comprises a  $H_2$ -type ellipsoidal MO bridging two  $C_{alkane} 2sp^3$  HOs having the dimensional diagram shown in Figure 49.

ENERGIES OF THE  $CH_2$  GROUPS

The energies of each  $CH_2$  group of  $C_nH_{2n+2}$  are given by the substitution of the semiprincipal axes (Eqs. (14.595-14.596) and (14.599)) into the energy equations of dihydrogen carbide radical (Eqs. (13.510-13.514)), with the exception that  $E(C_{alkane}, 2sp^3)$  (Eq. (14.512)) replaces  $E(C, 2sp^3)$  in Eq. (13.514):

$$V_e = 2(0.91771) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -70.41425 \text{ eV} \quad (14.610)$$

$$V_p = \frac{2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = 25.78002 \text{ eV} \quad (14.611)$$

$$T = 2(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 21.06675 \text{ eV} \quad (14.612)$$

$$V_m = 2(0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -10.53337 \text{ eV} \quad (14.613)$$

$$10 \quad E_{T_{alkane}}(CH_2) = -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 \text{ eV} = -49.66493 \text{ eV} \quad (14.614)$$

where  $E_{T_{alkane}}(CH_2)$  is given by Eq. (14.592) which is reiteratively matched to Eq. (13.496) within five-significant-figure round off error.

15 VIBRATION OF THE  $^{12}CH_2$  GROUPS

The vibrational energy levels of the  $C-H$  bonds of  $CH_2$  in  $C_nH_{2n+2}$  may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF THE  $^{12}CH_2$  GROUPS

The equations of the radiation reaction force of the methylene groups in  $C_nH_{2n+2}$  are the same as those of the dihydrogen carbide radical with the substitution of the methylene-group

parameters. Using Eq. (13.515), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 2.42751 \times 10^{16} \text{ rad/s} \quad (14.615)$$

where  $b$  is given by Eq. (14.599). The kinetic energy,  $E_K$ , is given by Planck's equation 5 (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.42751 \times 10^{16} \text{ rad/s} = 15.97831 \text{ eV} \quad (14.616)$$

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (14.616) for  $\bar{E}_K$  gives the Doppler energy of the electrons of each of the 10 three bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -31.63537 \text{ eV} \sqrt{\frac{2e(15.97831 \text{ eV})}{m_e c^2}} = -0.25017 \text{ eV} \quad (14.617)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $CH_2$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic 15 oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (14.617) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of each  $C-H$  bond. Using  $\omega_e$  given by Eq. (13.458) for  $\bar{E}_{Kvib}$  of the transition state having two independent bonds,  $\bar{E}'_{alkane osc} (^{12}CH_2)$  per bond is

$$\bar{E}'_{alkane osc} (^{12}CH_2) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (14.618)$$

$$20 \quad \bar{E}'_{alkane osc} (^{12}CH_2) = -0.25017 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) = -0.07251 \text{ eV} \quad (14.619)$$

Given that the vibration and reentrant oscillation is for two  $C-H$  bonds,  $\bar{E}_{alkane osc} (^{12}CH_2)$ , is:

$$\bar{E}_{alkane osc} (^{12}CH_2) = 2 \left( \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) = 2 \left( -0.25017 \text{ eV} + \frac{1}{2} (0.35532 \text{ eV}) \right) = -0.14502 \text{ eV}$$

TOTAL BOND ENERGIES OF THE  $^{12}\text{CH}_2$  GROUPS

$E_{alkaneT+osc} (^{12}\text{CH}_2)$ , the total energy of each  $^{12}\text{CH}_2$  group including the Doppler term, is given

5 by the sum of  $E_{T_{alkane}} (CH_2)$  (Eq. (14.614)) and  $\bar{E}_{alkane\ osc} (^{12}\text{CH}_2)$  given by Eq. (14.620):

$$\begin{aligned}
 E_{alkaneT+osc} (CH_2) &= V_e + T + V_m + V_p + E(C_{alkane}, 2sp^3) + \bar{E}_{alkane\ osc} (^{12}\text{CH}_2) \\
 &= E_{T_{alkane}} (CH_2) + \bar{E}_{alkane\ osc} (^{12}\text{CH}_2) \\
 E_{alkaneT+osc} (^{12}\text{CH}_2) &= \left\{ \left( \frac{-2e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 \text{ eV} \right) \right. \\
 &\quad \left. - 2 \left( (31.63536831 \text{ eV}) \sqrt{\frac{2\hbar \sqrt{\frac{3}{4} \frac{e^2}{4\pi\epsilon_0 b^3}}}{m_e c^2}} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \right\} \\
 &= -49.66493 \text{ eV} - 2 \left( 0.25017 \text{ eV} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)
 \end{aligned} \tag{14.621}$$

(14.622)

From Eqs. (14.620-14.622), the total energy of each  $^{12}\text{CH}_2$  is

$$\begin{aligned}
 E_{alkaneT+osc} (^{12}\text{CH}_2) &= -49.66493 \text{ eV} + \bar{E}_{alkane\ osc} (^{12}\text{CH}_2) \\
 &= -49.66493 \text{ eV} - 2 \left( 0.25017 \text{ eV} - \frac{1}{2} (0.35532 \text{ eV}) \right) \\
 &= -49.80996 \text{ eV}
 \end{aligned} \tag{14.623}$$

10

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

The derivation of the total  $\text{CH}_2$  bond dissociation energy,  $E_{D_{alkane}} (^{12}\text{CH}_2)$  follows from that of the bond dissociation energy of dihydrogen carbide radical,  $E_D (^{12}\text{CH}_2)$ , given by Eqs. (13.524-13.527).  $E_{D_{alkane}} (^{12}\text{CH}_2)$  is given by the sum of the initial  $\text{C}2sp^3$  HO energy, 15  $E(C, 2sp^3)$  (Eq. (14.146)), and two times the energy of the hydrogen atom,  $E(H)$  (Eq. (13.154)), minus the sum of  $E_{alkaneT+osc} (^{12}\text{CH}_2)$  (Eq. (14.623)) and  $E(\text{magnetic})$  (Eq. 13.524)):

430

$$E_{D_{alkane}}(^{12}CH_2) = E(C, 2sp^3) + 2E(H) - E_{alkaneT+osc}(^{12}CH_2) - E(magnetic) \quad (14.624)$$

Thus, the total  $^{12}CH_2$  bond dissociation energy,  $E_{D_{alkane}}(^{12}CH_2)$  is

$$\begin{aligned} E_{D_{alkane}}(^{12}CH_2) &= -(14.63489 \text{ eV} + 2(13.59844 \text{ eV})) - (E_{alkaneT+osc}(^{12}CH_2) + E(magnetic)) \\ &= -41.83177 \text{ eV} - (-49.80996 \text{ eV} + 0.14803 \text{ eV}) \\ &= 7.83016 \text{ eV} \end{aligned} \quad (14.625)$$

5

### SUM OF THE ENERGIES OF THE $C-C$ $\sigma$ MOs AND THE HOs OF CONTINUOUS-CHAIN ALKANES

The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  of the  $C-C$ -bond MOs are the same as those of the  $CH$  MO except that energy of the  $C_{alkane}2sp^3$  HO is used. The energies of each  $C-C$ -bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.523-14.524) and (14.528)) into the energy equations of the  $CH$  MO (Eqs. (13.449-13.453)), with the exception that  $E(C_{alkane}, 2sp^3)$  (Eq. (14.512)) replaces  $E(C, 2sp^3)$  in Eq. (13.453). The total number of  $C-C$  bonds of  $C_nH_{2n+2}$  is  $n-1$ . Thus, the energies of the  $n-1$  bonds is given by

$$15 \quad V_e = (n-1)(0.91771) \frac{-2e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -(n-1)28.79214 \text{ eV} \quad (14.626)$$

$$V_p = \frac{(n-1)e^2}{8\pi\epsilon_0\sqrt{a^2-b^2}} = (n-1)9.33352 \text{ eV} \quad (14.627)$$

$$T = (n-1)(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = (n-1)6.77464 \text{ eV} \quad (14.628)$$

$$V_m = (n-1)(0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -(n-1)3.38732 \text{ eV} \quad (14.629)$$

$$\begin{aligned} E_{T_{alkane}}(C-C, \sigma) &= -\frac{(n-1)e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 \text{ eV} \\ &= -(n-1)31.63537 \text{ eV} \end{aligned} \quad (14.630)$$

20

where  $E_{T_{alkane}}(C-C, \sigma)$  is the total energy of the  $C-C$   $\sigma$  MOs given by Eq. (14.520) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

Since there are two carbon atoms per bond, the number of  $C-C$  bonds is  $n-1$ , and the energy change of each  $C2sp^3$  shell due to the decrease in radius with the formation of each  $C-C$ -bond MO is  $E_{T_{alkane}}(C-C, 2sp^3)$  (Eq. (14.517)), the total energy of the  $C-C$ -bond MOs,  $E_{T_{alkane}}(C-C)$ , is given by the sum of  $2(n-1)E_{T_{alkane}}(C-C, 2sp^3)$  and  $E_{T_{alkane}}(C-C, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (14.630):

$$\begin{aligned}
 E_{T_{alkane}}(C-C) &= 2(n-1)E_{T_{alkane}}(C-C, 2sp^3) + E_{T_{alkane}}(C-C, \sigma) \\
 &= (n-1) \left[ 2(-0.92918 \text{ eV}) + \left( -\frac{e^2}{8\pi\epsilon_0\sqrt{aa_0}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{aa_0}}{a - \sqrt{aa_0}} - 1 \right] \right) \right] \\
 &= (n-1) \left( 2(-0.92918 \text{ eV}) + (-31.63537 \text{ eV}) \right) \\
 &= -(n-1)33.49373 \text{ eV}
 \end{aligned} \tag{14.631}$$

## VIBRATION OF CONTINUOUS-CHAIN ALKANES

The vibrational energy levels of the  $C-C$  bonds of  $C_nH_{2n+2}$  may be solved as  $n-1$  sets of coupled carbon harmonic oscillators wherein each carbon is further coupled to two or three equivalent  $H$  harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE $C-C$ -BOND MOs OF CONTINUOUS-CHAIN ALKANES

The equations of the radiation reaction force of each symmetrical  $C-C$ -bond MO are given by Eqs. (11.231-11.233), except the force-constant factor is 0.5 based on the force constant  $k'$  of Eq. (14.152), and the  $C-C$ -bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.5e^2}{4\pi\epsilon_0 a^3}} = 9.43699 \times 10^{15} \text{ rad/s} \tag{14.632}$$

where  $a$  is given by Eq. (14.523). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 9.43699 \times 10^{15} \text{ rad/s} = 6.21159 \text{ eV} \quad (14.633)$$

In Eq. (11.181), substitution of  $E_{T_{alkane}}(C-C)$  (Eq. (14.631)) with  $n=2$  for  $E_{hv}$ , the mass of the electron,  $m_e$ , for  $M$ , and the kinetic energy given by Eq. (14.633) for  $\bar{E}_K$  gives the Doppler energy of the electrons of each of the bonds for the reentrant orbit:

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{Mc^2}} = -33.49373 \text{ eV} \sqrt{\frac{2e(6.21159 \text{ eV})}{m_e c^2}} = -0.16515 \text{ eV} \quad (14.634)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of each  $C-C$  bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\bar{E}_{osc}$ , is given by the sum of the corresponding energies,  $\bar{E}_D$  given by Eq. (14.634) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of each  $C-C$  bond. Using the ethane experimental  $C-C$   $E_{vib}(\nu_3)$  of  $993 \text{ cm}^{-1}$  ( $0.12312 \text{ eV}$ ) [10] for  $\bar{E}_{Kvib}$  of the transition state having  $n-1$  independent bonds,  $\bar{E}'_{alkane\ osc}(C-C, \sigma)$  per bond is

$$\bar{E}'_{alkane\ osc}(C-C, \sigma) = \bar{E}_D + \bar{E}_{Kvib} = \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \quad (14.635)$$

$$\bar{E}'_{alkane\ osc}(C-C, \sigma) = -0.16515 \text{ eV} + \frac{1}{2} (0.12312 \text{ eV}) = -0.10359 \text{ eV} \quad (14.636)$$

Given that the vibration and reentrant oscillation is for  $n-1$   $C-C$  bonds,  $\bar{E}_{alkane\ osc}(C-C, \sigma)$ , is:

$$\begin{aligned} \bar{E}_{alkane\ osc}(C-C, \sigma) &= (n-1) \left( \bar{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \\ &= (n-1) \left( -0.16515 \text{ eV} + \frac{1}{2} (0.12312 \text{ eV}) \right) \\ &= -(n-1) 0.10359 \text{ eV} \end{aligned} \quad (14.637)$$



# TOTAL ENERGIES OF THE C-C-BOND MOs OF CONTINUOUS-CHAIN ALKANES

$E_{alkaneT+osc}(C-C)$ , the total energy of the  $n-1$  bonds of the C-C-bond MOs including the Doppler term, is given by the sum of  $E_{T_{alkane}}(C-C)$  (Eq. (14.631)) and  $\bar{E}_{alkane\ osc}(C-C, \sigma)$  given by Eq. (14.637):

$$\begin{aligned} E_{alkaneT+osc}(C-C) &= \left( (n-1) \left( V_e + T + V_m + V_p + E(C_{alkane}, 2sp^3) \right) + \bar{E}_{alkane\ osc}(C-C, \sigma) \right) \\ &= E_{T_{alkane}}(C-C, \sigma) + 2(n-1) E_{T_{alkane}}(C-C, 2sp^3) + \bar{E}_{alkane\ osc}(C-C, \sigma) \\ &= E_{T_{alkane}}(C-C) + \bar{E}_{alkane\ osc}(C-C, \sigma) \end{aligned} \quad (14.638)$$

$$\begin{aligned} E_{alkaneT+osc}(C-C) &= (n-1) \left\{ \left( \frac{-e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \right) \right. \\ &\quad \left. -15.56407\ eV + 2E_{T_{alkane}}(C-C, 2sp^3) \right\} \\ &\quad \left\{ \left( 1 + \sqrt{\frac{2\hbar \sqrt{\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} \right) + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right\} \\ &= (n-1) \left( -33.49373\ eV - 0.16515\ eV + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \end{aligned} \quad (14.639)$$

From Eqs. (14.637-14.639), the total energy of the  $n-1$  bonds of the C-C-bond MOs is

$$\begin{aligned} E_{alkaneT+osc}(C-C) &= (n-1) \left( -31.63537\ eV + 2E_{T_{alkane}}(C-C, 2sp^3) \right) + \bar{E}_{alkane\ osc}(C-C, \sigma) \\ &= (n-1) \left( -31.63537\ eV + 2(-0.92918\ eV) \right) \\ &\quad \left( -0.16515\ eV + \frac{1}{2} (0.12312\ eV) \right) \\ &= -(n-1) 33.59732\ eV \end{aligned} \quad (14.640)$$

where the experimental  $E_{vib}$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

## TOTAL BOND ENERGY OF THE C-C BONDS OF CONTINUOUS-CHAIN ALKANES

Since there are two carbon atoms per bond and the number of C-C bonds is  $n-1$ , the total bond energy of the C-C bonds of  $C_nH_{2n+2}$ ,  $E_D(C-C)_{n-1}$ , is given by  $2(n-1)E(C, 2sp^3)$  minus  $E_{alkaneT+osc}(C-C)$  (Eq. (14.640)) where  $E(C, 2sp^3)$  (Eq. (14.146)) is the initial energy of each  $C2sp^3$  HO of the  $CH_3$  and  $CH_2$  groups that bond to the C-C bonds. Thus, the total dissociation energy of the C-C bonds of  $C_nH_{2n+2}$ , is

$$\begin{aligned} E_D(C-C)_{n-1} &= 2(n-1)(E(C, 2sp^3)) - (E_{alkaneT+osc}(C-C)) \\ &= 2(n-1)(-14.63489 \text{ eV}) - (n-1)(-33.59732 \text{ eV}) \\ &= (n-1)(2(-14.63489 \text{ eV}) - (-33.59732 \text{ eV})) \\ &= (n-1)(4.32754 \text{ eV}) \end{aligned} \quad (14.641)$$

## 10 TOTAL ENERGY OF CONTINUOUS-CHAIN ALKANES

$E_D(C_nH_{2n+2})$ , the total bond dissociation energy of  $C_nH_{2n+2}$ , is given as the sum of the energy components due to the two methyl groups,  $n-2$  methylene groups, and  $n-1$  C-C bonds where each energy component is given by Eqs. (14.590), (14.625), and (14.641), respectively. Thus, the total bond dissociation energy of  $C_nH_{2n+2}$  is

$$\begin{aligned} E_D(C_nH_{2n+2}) &= E_D(C-C)_{n-1} + 2E_{D_{alkane}}(^{12}CH_3) + (n-2)E_{D_{alkane}}(^{12}CH_2) \\ &= (n-1)(4.32754 \text{ eV}) + 2(12.49186 \text{ eV}) + (n-2)(7.83016 \text{ eV}) \end{aligned} \quad (14.642)$$

The experimental total bond dissociation energy of  $C_nH_{2n+2}$ ,  $E_{D_{exp}}(C_nH_{2n+2})$ , is given by the negative difference between the enthalpy of its formation ( $\Delta H_f(C_nH_{2n+2}(gas))$ ) and the sum of the enthalpy of the formation of the reactant gaseous carbons ( $\Delta H_f(C(gas))$ ) and hydrogen ( $\Delta H_f(H(gas))$ ) atoms:

$$\begin{aligned} E_{D_{exp}}(C_nH_{2n+2}) &= -\left\{ \Delta H_f(C_nH_{2n+2}(gas)) - \left[ n\Delta H_f(C(gas)) + (2n+2)\Delta H_f(H(gas)) \right] \right\} \\ &= -\left\{ \Delta H_f(C_nH_{2n+2}(gas)) - \left[ n7.42774 \text{ eV} + (2n+2)2.259353 \text{ eV} \right] \right\} \end{aligned} \quad (14.643)$$

where the heats of formation atomic carbon and hydrogen gas are given by [17-18]

$$\Delta H_f(C(gas)) = 716.68 \text{ kJ/mole } (7.42774 \text{ eV/molecule}) \quad (14.644)$$

$$\Delta H_f(H(gas)) = 217.998 \text{ kJ/mole } (2.259353 \text{ eV/molecule}) \quad (14.645)$$

Using the corresponding experimental  $\Delta H_f(C_nH_{2n+2}(gas))$  [18],  $E_D(C_nH_{2n+2})$  was determined from propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and octadecane in the corresponding sections, and the results of the determination of the total energies are given in Table 14.1. The calculated results are based  
 5 on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

Using the results for  $C_nH_{2n+2}$  and the functional groups as basis sets that are linearly combined, the exact solution for the dimensional parameters, charge density functions, and energies of all molecules can be obtained. For example, one or more of the hydrogen atoms  
 10 of the solution for  $C_nH_{2n+2}$  can be substituted with one or more of the previously solved functional groups or derivative functional groups to give a desired molecule. The solution is given by energy matching each group to  $C_nH_{2n+2}$ . Substitution of one or more  $H$ 's of  $C_nH_{2n+2}$  with functional groups from the list of  $CH_3$ , other  $C_nH_{2n+2}$  groups,  $H_2C=CH_2$ ,  $HC\equiv CH$ ,  $F$ ,  $Cl$ ,  $O$ ,  $OH$ ,  $NH$ ,  $NH_2$ ,  $CN$ ,  $NO$ ,  $NO_2$ ,  $CO$ ,  $CO_2$ , and  $C_6H_6$  give the  
 15 solutions of branched alkanes, alkenes, and alkynes, alkyl halides, ethers, alcohols, amides, amines, nitriles, alkyl nitrosos, alkyl nitrates, aldehydes, ketones, carboxylic acids, esters, and substituted aromatics.

### PROPANE ( $C_3H_8$ )

20 Using Eq. (14.642) with  $n = 3$ , the total bond dissociation energy of  $C_3H_8$  is

$$\begin{aligned} E_D(C_3H_8) &= E_D(C-C)_2 + 2E_{D_{alkane}}(^{12}CH_3) + E_{D_{alkane}}(^{12}CH_2) \\ &= (2)(4.32754 \text{ eV}) + (2)(12.49186 \text{ eV}) + (1)(7.83016 \text{ eV}) \quad (14.646) \\ &= 41.46896 \text{ eV} \end{aligned}$$

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_3H_8$ ,  $E_{D_{exp}}(C_3H_8)$ , given by the negative difference between the enthalpy of its formation ( $\Delta H_f(C_3H_8(gas)) = -1.0758 \text{ eV}$ ) [18] and the sum of the enthalpy of the formation of the  
 25 gaseous carbons ( $\Delta H_f(C(gas))$ ) and hydrogen ( $\Delta H_f(H(gas))$ ) atoms is

$$\begin{aligned} E_{D_{exp}}(C_3H_8) &= -\left\{ \Delta H_f(C_3H_8(gas)) - \left[ 3\Delta H_f(C(gas)) + 8\Delta H_f(H(gas)) \right] \right\} \\ &= -\left\{ -1.0758 \text{ eV} - \left[ (3)7.42774 \text{ eV} + (8)2.259353 \text{ eV} \right] \right\} \quad (14.647) \\ &= 41.434 \text{ eV} \end{aligned}$$

The charge-density of the  $C_3H_8$  molecular orbital (MO) comprising a linear combination of two methyl groups and one methylene group is shown in Figure 50.

### BUTANE ( $C_4H_{10}$ )

5 Using Eq. (14.642) with  $n = 4$ , the total bond dissociation energy of  $C_4H_{10}$  is

$$\begin{aligned} E_D(C_4H_{10}) &= E_D(C-C)_3 + 2E_{D_{alkane}}(^{12}CH_3) + 2E_{D_{alkane}}(^{12}CH_2) \\ &= (3)(4.32754 \text{ eV}) + (2)(12.49186 \text{ eV}) + (2)(7.83016 \text{ eV}) \\ &= 53.62666 \text{ eV} \end{aligned} \quad (14.648)$$

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_4H_{10}$ ,  $E_{D_{exp}}(C_4H_{10})$ , given by the negative difference between the enthalpy of its formation ( $\Delta H_f(C_4H_{10}(gas)) = -1.3028 \text{ eV}$ ) [18] and the sum of the enthalpy of the formation of the  
10 gaseous carbons ( $\Delta H_f(C(gas))$ ) and hydrogen ( $\Delta H_f(H(gas))$ ) atoms is

$$\begin{aligned} E_{D_{exp}}(C_4H_{10}) &= -\left\{ \Delta H_f(C_4H_{10}(gas)) - \left[ 4\Delta H_f(C(gas)) + 10\Delta H_f(H(gas)) \right] \right\} \\ &= -\left\{ -1.3028 \text{ eV} - \left[ (4)7.42774 \text{ eV} + (10)2.259353 \text{ eV} \right] \right\} \\ &= 53.61 \text{ eV} \\ (14.649) \end{aligned}$$

The charge-density of the  $C_4H_{10}$  molecular orbital (MO) comprising a linear combination of two methyl and two methylene groups is shown in Figure 51.

15

### PENTANE ( $C_5H_{12}$ )

Using Eq. (14.642) with  $n = 5$ , the total bond dissociation energy of  $C_5H_{12}$  is

$$\begin{aligned} E_D(C_5H_{12}) &= E_D(C-C)_4 + 2E_{D_{alkane}}(^{12}CH_3) + 3E_{D_{alkane}}(^{12}CH_2) \\ &= (4)(4.32754 \text{ eV}) + (2)(12.49186 \text{ eV}) + (3)(7.83016 \text{ eV}) \\ &= 65.78436 \text{ eV} \end{aligned} \quad (14.650)$$

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_5H_{12}$ ,  $E_{D_{exp}}(C_5H_{12})$ ,  
20 given by the negative difference between the enthalpy of its formation ( $\Delta H_f(C_5H_{12}(gas)) = -1.5225 \text{ eV}$ ) [18] and the sum of the enthalpy of the formation of the gaseous carbons ( $\Delta H_f(C(gas))$ ) and hydrogen ( $\Delta H_f(H(gas))$ ) atoms is

$$\begin{aligned}
 E_{D_{\text{exp}}}(C_5H_{12}) &= -\left\{\Delta H_f(C_5H_{12}(gas)) - \left[5\Delta H_f(C(gas)) + 12\Delta H_f(H(gas))\right]\right\} \\
 &= -\left\{-1.5225 \text{ eV} - \left[(5)7.42774 \text{ eV} + (12)2.259353 \text{ eV}\right]\right\} \quad (14.651) \\
 &= 65.77 \text{ eV}
 \end{aligned}$$

The charge-density of the  $C_5H_{12}$  molecular orbital (MO) comprising a linear combination of two methyl and three methylene groups is shown in Figure 52.

## 5 HEXANE ( $C_6H_{14}$ )

Using Eq. (14.642) with  $n = 6$ , the total bond dissociation energy of  $C_6H_{14}$  is

$$\begin{aligned}
 E_D(C_6H_{14}) &= E_D(C-C)_5 + 2E_{D_{\text{alkane}}}(^{12}CH_3) + 4E_{D_{\text{alkane}}}(^{12}CH_2) \\
 &= (5)(4.32754 \text{ eV}) + (2)(12.49186 \text{ eV}) + (4)(7.83016 \text{ eV}) \quad (14.652) \\
 &= 77.94206 \text{ eV}
 \end{aligned}$$

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_6H_{14}$ ,  $E_{D_{\text{exp}}}(C_6H_{14})$ , given by the negative difference between the enthalpy of its formation  
 10 ( $\Delta H_f(C_6H_{14}(gas)) = -1.7298 \text{ eV}$ ) [18] and the sum of the enthalpy of the formation of the gaseous carbons ( $\Delta H_f(C(gas))$ ) and hydrogen ( $\Delta H_f(H(gas))$ ) atoms is

$$\begin{aligned}
 E_{D_{\text{exp}}}(C_6H_{14}) &= -\left\{\Delta H_f(C_6H_{14}(gas)) - \left[6\Delta H_f(C(gas)) + 14\Delta H_f(H(gas))\right]\right\} \\
 &= -\left\{-1.7298 \text{ eV} - \left[(6)7.42774 \text{ eV} + (14)2.259353 \text{ eV}\right]\right\} \\
 &= 77.93 \text{ eV} \\
 (14.653)
 \end{aligned}$$

The charge-density of the  $C_6H_{14}$  molecular orbital (MO) comprising a linear combination of  
 15 two methyl and four methylene groups is shown in Figure 53.

## HEPTANE ( $C_7H_{16}$ )

Using Eq. (14.642) with  $n = 7$ , the total bond dissociation energy of  $C_7H_{16}$  is

$$\begin{aligned}
 E_D(C_7H_{16}) &= E_D(C-C)_6 + 2E_{D_{\text{alkane}}}(^{12}CH_3) + 5E_{D_{\text{alkane}}}(^{12}CH_2) \\
 &= (6)(4.32754 \text{ eV}) + (2)(12.49186 \text{ eV}) + (5)(7.83016 \text{ eV}) \quad (14.654) \\
 &= 90.09976 \text{ eV}
 \end{aligned}$$

20 Using Eq. (14.643), the experimental total bond dissociation energy of  $C_7H_{16}$ ,  $E_{D_{\text{exp}}}(C_7H_{16})$ , given by the negative difference between the enthalpy of its formation

$(\Delta H_f(C_7H_{16}(gas)) = -1.9443 \text{ eV})$  [18] and the sum of the enthalpy of the formation of the gaseous carbons  $(\Delta H_f(C(gas)))$  and hydrogen  $(\Delta H_f(H(gas)))$  atoms is

$$\begin{aligned} E_{D_{\text{exp}}}(C_7H_{16}) &= -\left\{\Delta H_f(C_7H_{16}(gas)) - \left[7\Delta H_f(C(gas)) + 16\Delta H_f(H(gas))\right]\right\} \\ &= -\left\{-1.9443 \text{ eV} - \left[(7)7.42774 \text{ eV} + (16)2.259353 \text{ eV}\right]\right\} \\ &= 90.09 \text{ eV} \end{aligned}$$

(14.655)

- 5 The charge-density of the  $C_7H_{16}$  MO comprising a linear combination of two methyl and five methylene groups is shown in Figure 54.

### **OCTANE ( $C_8H_{18}$ )**

Using Eq. (14.642) with  $n = 8$ , the total bond dissociation energy of  $C_8H_{18}$  is

$$\begin{aligned} E_D(C_8H_{18}) &= E_D(C-C)_7 + 2E_{D_{\text{alkane}}}(^{12}CH_3) + 6E_{D_{\text{alkane}}}(^{12}CH_2) \\ 10 \quad &= (7)(4.32754 \text{ eV}) + (2)(12.49186 \text{ eV}) + (6)(7.83016 \text{ eV}) \quad (14.656) \\ &= 102.25746 \text{ eV} \end{aligned}$$

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_8H_{18}$ ,  $E_{D_{\text{exp}}}(C_8H_{18})$ , given by the negative difference between the enthalpy of its formation  $(\Delta H_f(C_8H_{18}(gas)) = -2.1609 \text{ eV})$  [18] and the sum of the enthalpy of the formation of the gaseous carbons  $(\Delta H_f(C(gas)))$  and hydrogen  $(\Delta H_f(H(gas)))$  atoms is

$$\begin{aligned} E_{D_{\text{exp}}}(C_8H_{18}) &= -\left\{\Delta H_f(C_8H_{18}(gas)) - \left[8\Delta H_f(C(gas)) + 18\Delta H_f(H(gas))\right]\right\} \\ 15 \quad &= -\left\{-2.1609 \text{ eV} - \left[(8)7.42774 \text{ eV} + (18)2.259353 \text{ eV}\right]\right\} \\ &= 102.25 \text{ eV} \end{aligned}$$

(14.657)

The charge-density of the  $C_8H_{18}$  MO comprising a linear combination of two methyl and six methylene groups is shown in Figure 55.

### 20 **NONANE ( $C_9H_{20}$ )**

Using Eq. (14.642) with  $n = 9$ , the total bond dissociation energy of  $C_9H_{20}$  is

439

$$\begin{aligned}
 E_D(C_9H_{20}) &= E_D(C-C)_8 + 2E_{D_{alkane}}(^{12}CH_3) + 7E_{D_{alkane}}(^{12}CH_2) \\
 &= (8)(4.32754 \text{ eV}) + (2)(12.49186 \text{ eV}) + (7)(7.83016 \text{ eV}) \\
 &= 114.41516 \text{ eV}
 \end{aligned} \tag{14.658}$$

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_9H_{20}$ ,  $E_{D_{exp}}(C_9H_{20})$ , given by the negative difference between the enthalpy of its formation ( $\Delta H_f(C_9H_{20}(gas)) = -2.3651 \text{ eV}$ ) [18] and the sum of the enthalpy of the formation of the

5 gaseous carbons ( $\Delta H_f(C(gas))$ ) and hydrogen ( $\Delta H_f(H(gas))$ ) atoms is

$$\begin{aligned}
 E_{D_{exp}}(C_9H_{20}) &= -\left\{\Delta H_f(C_9H_{20}(gas)) - [9\Delta H_f(C(gas)) + 20\Delta H_f(H(gas))]\right\} \\
 &= -\left\{-2.3651 \text{ eV} - [(9)7.42774 \text{ eV} + (20)2.259353 \text{ eV}]\right\} \\
 &= 114.40 \text{ eV}
 \end{aligned} \tag{14.659}$$

The charge-density of the  $C_9H_{20}$  MO comprising a linear combination of two methyl and seven methylene groups is shown in Figure 56.

10

### DECANE ( $C_{10}H_{22}$ )

Using Eq. (14.642) with  $n = 10$ , the total bond dissociation energy of  $C_{10}H_{22}$  is

$$\begin{aligned}
 E_D(C_{10}H_{22}) &= E_D(C-C)_9 + 2E_{D_{alkane}}(^{12}CH_3) + 8E_{D_{alkane}}(^{12}CH_2) \\
 &= (9)(4.32754 \text{ eV}) + (2)(12.49186 \text{ eV}) + (8)(7.83016 \text{ eV}) \\
 &= 126.57286 \text{ eV}
 \end{aligned} \tag{14.660}$$

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_{10}H_{22}$ ,  $E_{D_{exp}}(C_{10}H_{22})$ , given by the negative difference between the enthalpy of its formation ( $\Delta H_f(C_{10}H_{22}(gas)) = -2.5858 \text{ eV}$ ) [18] and the sum of the enthalpy of the formation of the

15 gaseous carbons ( $\Delta H_f(C(gas))$ ) and hydrogen ( $\Delta H_f(H(gas))$ ) atoms is

$$\begin{aligned}
 E_{D_{exp}}(C_{10}H_{22}) &= -\left\{\Delta H_f(C_{10}H_{22}(gas)) - [10\Delta H_f(C(gas)) + 22\Delta H_f(H(gas))]\right\} \\
 &= -\left\{-2.5858 \text{ eV} - [(10)7.42774 \text{ eV} + (22)2.259353 \text{ eV}]\right\} \\
 &= 126.57 \text{ eV}
 \end{aligned} \tag{14.661}$$

20 The charge-density of the  $C_{10}H_{22}$  molecular orbital (MO) comprising a linear combination of two methyl and eight methylene groups is shown in Figure 57.

**UNDECANE ( $C_{11}H_{24}$ )**

Using Eq. (14.642) with  $n = 11$ , the total bond dissociation energy of  $C_{11}H_{24}$  is

$$\begin{aligned} E_D(C_{11}H_{24}) &= E_D(C-C)_{10} + 2E_{D_{alkane}}(^{12}CH_3) + 9E_{D_{alkane}}(^{12}CH_2) \\ &= (10)(4.32754 \text{ eV}) + (2)(12.49186 \text{ eV}) + (9)(7.83016 \text{ eV}) \quad (14.662) \\ &= 138.73056 \text{ eV} \end{aligned}$$

5 Using Eq. (14.643), the experimental total bond dissociation energy of  $C_{11}H_{24}$ ,  $E_{D_{exp}}(C_{11}H_{24})$ , given by the negative difference between the enthalpy of its formation ( $\Delta H_f(C_{11}H_{24}(gas) = -2.8066 \text{ eV})$ ) [18] and the sum of the enthalpy of the formation of the gaseous carbons ( $\Delta H_f(C(gas))$ ) and hydrogen ( $\Delta H_f(H(gas))$ ) atoms is

$$\begin{aligned} E_{D_{exp}}(C_{11}H_{24}) &= -\left\{ \Delta H_f(C_{11}H_{24}(gas)) - [11\Delta H_f(C(gas)) + 24\Delta H_f(H(gas))] \right\} \\ &= -\left\{ -2.8066 \text{ eV} - [(11)7.42774 \text{ eV} + (24)2.259353 \text{ eV}] \right\} \\ &= 138.736 \text{ eV} \end{aligned}$$

10 (14.663)

The charge-density of the  $C_{11}H_{24}$  MO comprising a linear combination of two methyl and nine methylene groups is shown in Figure 58.

**15 DODECANE ( $C_{12}H_{26}$ )**

Using Eq. (14.642) with  $n = 12$ , the total bond dissociation energy of  $C_{12}H_{26}$  is

$$\begin{aligned} E_D(C_{12}H_{26}) &= E_D(C-C)_{11} + 2E_{D_{alkane}}(^{12}CH_3) + 10E_{D_{alkane}}(^{12}CH_2) \\ &= (11)(4.32754 \text{ eV}) + (2)(12.49186 \text{ eV}) + (10)(7.83016 \text{ eV}) \quad (14.664) \\ &= 150.88826 \text{ eV} \end{aligned}$$

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_{12}H_{26}$ ,  $E_{D_{exp}}(C_{12}H_{26})$ , given by the negative difference between the enthalpy of its formation ( $\Delta H_f(C_{12}H_{26}(gas) = -2.9994 \text{ eV})$ ) [18] and the sum of the enthalpy of the formation of the gaseous carbons ( $\Delta H_f(C(gas))$ ) and hydrogen ( $\Delta H_f(H(gas))$ ) atoms is

20



$$\begin{aligned}
 E_{D_{\text{exp}}}(C_{12}H_{26}) &= -\left\{\Delta H_f(C_{12}H_{26}(\text{gas})) - \left[12\Delta H_f(C(\text{gas})) + 26\Delta H_f(H(\text{gas}))\right]\right\} \\
 &= -\left\{-2.9994 \text{ eV} - \left[(12)7.42774 \text{ eV} + (26)2.259353 \text{ eV}\right]\right\} \quad (14.665) \\
 &= 150.88 \text{ eV}
 \end{aligned}$$

The charge-density of the  $C_{12}H_{26}$  MO comprising a linear combination of two methyl and ten methylene groups is shown in Figure 59.

## 5 OCTADECANE ( $C_{18}H_{38}$ )

Using Eq. (14.642) with  $n=18$ , the total bond dissociation energy of  $C_{18}H_{38}$  is

$$\begin{aligned}
 E_D(C_{18}H_{38}) &= E_D(C-C)_{17} + 2E_{D_{\text{alkane}}}(^{12}\text{CH}_3) + 16E_{D_{\text{alkane}}}(^{12}\text{CH}_2) \\
 &= (17)(4.32754 \text{ eV}) + (2)(12.49186 \text{ eV}) + (16)(7.83016 \text{ eV}) \quad (14.666) \\
 &= 223.83446 \text{ eV}
 \end{aligned}$$

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_{18}H_{38}$ ,  $E_{D_{\text{exp}}}(C_{18}H_{38})$ , given by the negative difference between the enthalpy of its formation  
 10 ( $\Delta H_f(C_{18}H_{38}(\text{gas})) = -4.2970 \text{ eV}$ ) [18] and the sum of the enthalpy of the formation of the  
 gaseous carbons ( $\Delta H_f(C(\text{gas}))$ ) and hydrogen ( $\Delta H_f(H(\text{gas}))$ ) atoms is

$$\begin{aligned}
 E_{D_{\text{exp}}}(C_{18}H_{38}) &= -\left\{\Delta H_f(C_{18}H_{38}(\text{gas})) - \left[18\Delta H_f(C(\text{gas})) + 38\Delta H_f(H(\text{gas}))\right]\right\} \\
 &= -\left\{-4.2970 \text{ eV} - \left[(18)7.42774 \text{ eV} + (38)2.259353 \text{ eV}\right]\right\} \\
 &= 223.85 \text{ eV} \\
 &\quad (14.667)
 \end{aligned}$$

The charge-density of the  $C_{18}H_{38}$  molecular orbital (MO) comprising a linear combination of  
 15 two methyl and sixteen methylene groups is shown in Figure 60.

Table 14.1. The calculated and experimental bond parameters of  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{CH}_3\text{CH}_3$ ,  $\text{CH}_2\text{CH}_2$ ,  $\text{CHCH}$ , benzene, propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and octadecane.

Parameter	Calculated	Experimental	Ref. for Exp.
$\text{CO}_2$ Bond Energy	5.49553 eV	5.51577 eV	7
$\text{CO}_2$ Bond Length	1.1616 Å	1.1600 Å	3

Parameter	442		
	Calculated	Experimental	Ref. for Exp.
$NO_2$ Bond Energy	3.1532 eV	3.161 eV	7
$NO_2$ Bond Length	1.1872 Å	1.193 Å	3
$NO_2$ Bond Angle	131.012°	134.1°	3
$H_3C-CH_3$ Bond Energy	3.90245 eV	3.8969 eV	7
$H_3C-CH_3$ Bond Length	1.53635 Å	1.5351 Å	3
$H-CH_2CH_3$ Bond Length	1.10822 Å	1.0940 Å	3
Ethane $H-C-H$ Bond Angle	107.44°	107.4°	8
Ethane $C-C-H$ Bond Angle	111.44°	111.17°	3
$H_2C=CH_2$ Bond Energy	7.55681 eV	7.597 eV	7
$H_2C=CH_2$ Bond Length	1.3405 Å	1.339 Å	3
$H-CHCH_2$ Bond Length	1.0826 Å	1.087 Å	3
Ethylene $H-C-H$ Bond Angle	116.31°	116.6°	11
Ethylene $C=C-H$ Bond Angle	121.85°	121.7°	11
$HC\equiv CH$ Bond Energy	10.07212 eV	10.0014 eV	7
$HC\equiv CH$ Bond Length	1.2007 Å	1.203 Å	3
$H-CCH$ Bond Length	1.0538 Å	1.060 Å	3
Acetylene $C\equiv C-H$ Bond Angle	180°	180°	6
$C_6H_6$ Total Bond Energy	57.2601 eV	57.26 eV	17-18
Benzene $C=C$ Bond Length	1.3914 Å	1.399 Å	3
$H-C_6H_5$ Bond Length	1.0933 Å	1.101 Å	3
$C_6H_6$ $C=C=C$ Bond Angle	120°	120°	13-15
$C_6H_6$ $C=C-H$ Bond Angle	120°	120°	13-15
$C_3H_8$ Total Bond Energy	41.46896 eV	41.434 eV	17-18
Propane $C-C$ Bond Length	1.5428 Å	1.532 Å	3
Propane $C-H$ Bond Length	1.1097 Å	1.107 Å	3
Alkane $H-C-H$ Bond Angle	109.50°	109.3°	19
Alkane $C-C-H$ Bond Angle	109.44°	109.3°	19
$C_4H_{10}$ Total Bond Energy	53.62666 eV	53.61 eV	17-18
Butane $C-C$ Bond Length	1.5428 Å	1.531 Å	3
Butane $C-H$ Bond Length	1.11713 Å	1.117 Å	3

Parameter	443		
	Calculated	Experimental	Ref. for Exp.
$C_3H_{12}$ Total Bond Energy	65.78436 eV	65.77 eV	17-18
$C_6H_{14}$ Total Bond Energy	77.94206 eV	77.93 eV	17-18
$C_7H_{16}$ Total Bond Energy	90.09976 eV	90.09 eV	17-18
$C_8H_{18}$ Total Bond Energy	102.25746 eV	102.25 eV	17-18
$C_9H_{20}$ Total Bond Energy	114.41516 eV	114.40 eV	17-18
$C_{10}H_{22}$ Total Bond Energy	126.57286 eV	126.57 eV	17-18
$C_{11}H_{24}$ Total Bond Energy	138.73056 eV	138.736 eV	17-18
$C_{12}H_{26}$ Total Bond Energy	150.88826 eV	150.88 eV	17-18
$C_{18}H_{38}$ Total Bond Energy	223.83446 eV	223.85 eV	17-18

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